

249

T H E S E S

présentées

A LA FACULTE DES SCIENCES D'ORSAY

Université de Paris

pour obtenir

le grade de Docteur ès Sciences Physiques

par

Affonso Augusto GUIDAO GOMES

1ère Thèse : Contribution à l'étude de la structure électronique des alliages de métaux de transition.

2ème Thèse : Propositions données par la Faculté.

Soutenues le 29 Juin 1967 devant la Commission d'Examen

MM. J. Friedel

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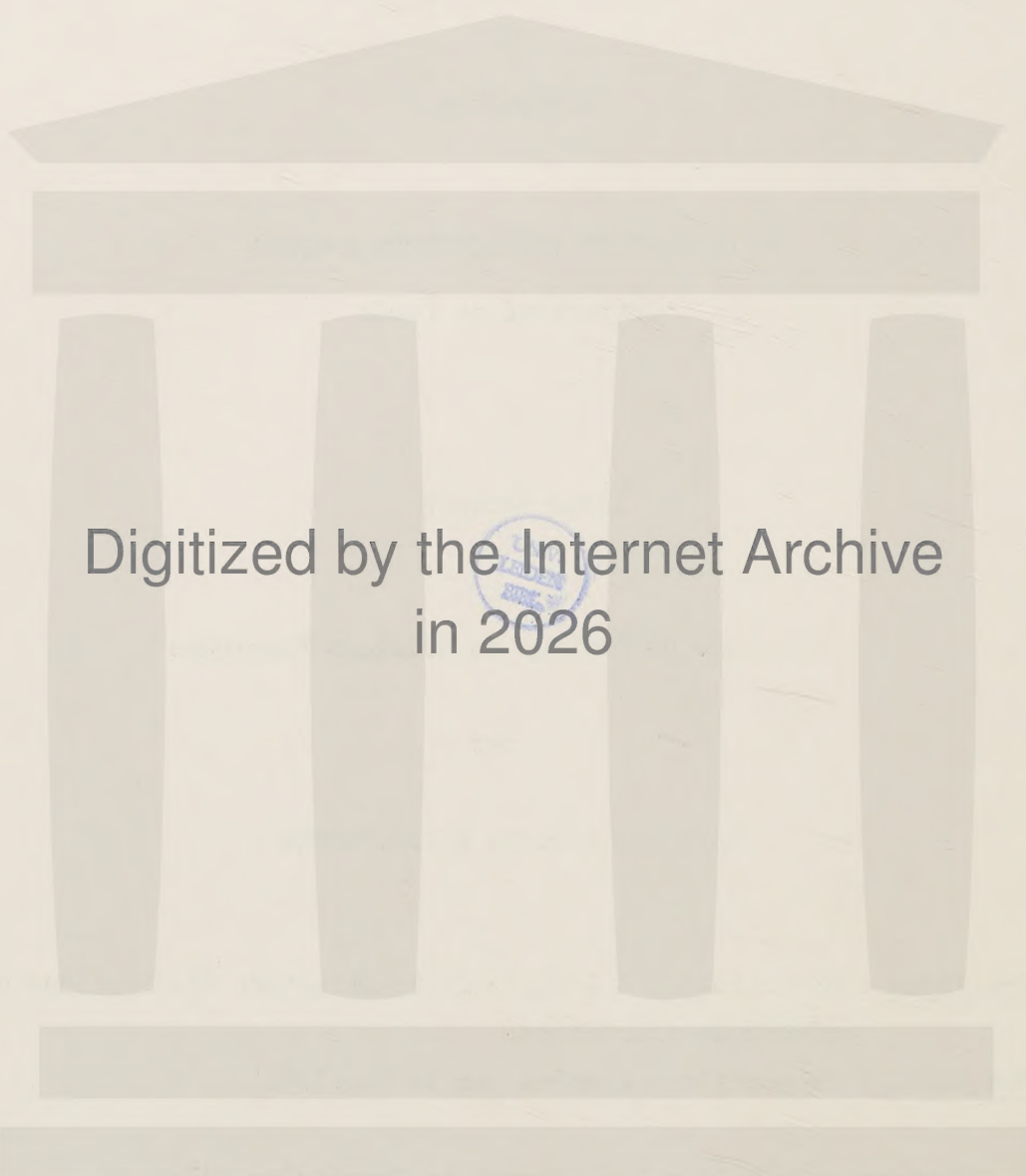
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A ma femme

Mobilis in mobili

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INTRODUCTION.

Ce travail a comme objectif l'étude théorique des perturbations introduites par des impuretés dans les métaux de transition.

Depuis quelques années l'étude expérimentale de ces alliages (surtout les alliages ferromagnétiques) a été particulièrement intense. Les grandeurs physiques mesurées ont été principalement les moments magnétiques des impuretés, le changement de moment magnétique moyen, la variation de chaleur spécifique électronique et quelques mesures des propriétés de transport.

Dans ce travail nous nous intéressons essentiellement à la limite des très faibles concentrations d'impuretés, où on peut considérer l'effet de chaque impureté isolément. D'un point de vue expérimental, cette situation très favorable pour la description théorique, pose un certain nombre de problèmes. L'obtention d'échantillons propres contenant très peu d'impuretés est parfois compliquée, et seulement quelques rares études ont été faites à des concentrations telles, qu'un modèle d'impuretés indépendantes puisse être valablement appliqué. En effet, la plupart des mesures existantes ont été faites à des concentrations assez fortes d'impuretés (technique suggérée par le modèle de bandes rigides). L'inconvénient de cette méthode expérimentale est d'introduire des effets collectifs (diffusions multiples des électrons de la matrice, etc ...) qui compliquent énormément la description théorique de ces alliages.

Même à la limite de faibles concentrations il existe des cas où les interactions à longue portée entre impuretés ne peuvent pas être négligées ; notre étude ne s'applique donc pas à ces situations.

STRUCTURE DE BANDES.

La structure électronique des métaux de transition est caractérisée par l'existence d'une bande étroite de caractère d qui chevauche une bande assez large dite s ou de conduction. Le faible recouvrement des orbitales atomiques d suggère l'approximation des liaisons fortes pour décrire la bande d , les électrons s seront par contre décrits dans l'approximation d'un gaz d'électrons libres.

Ce modèle simplifié, malgré son efficacité pour la description qualitative des propriétés de ces métaux et alliages est l'objet d'un certain nombre de critiques.

Parmi d'autres on néglige le manque d'orthogonalité entre les états s et d décrits de cette façon et en plus le mélange entre les deux bandes est complètement ignoré. La description de la perturbation introduite par une impureté dans un système où ces deux effets ont été inclus est extrêmement complexe.

On fera donc dans ce travail ces deux approximations mais en tenant bien présent l'esprit qualitatif de ce modèle.

DESCRIPTION DU POTENTIEL D'IMPURETE.

On adopte ici l'approximation d'électrons indépendants pour décrire le métal impur, le potentiel d'impureté étant donné par l'approximation de Hartree ou de Hartree-Fock.

La détermination du potentiel en fonction de la charge Z introduite par l'impureté et de la structure de bandes est difficile à faire en toute généralité. En effet il faudrait calculer la réponse du système à une perturbation donnée et la rendre self-consistente en déterminant le potentiel à partir des équations de Hartree ou de Hartree-Fock, ce calcul est extrêmement complexe en dehors d'une approximation de réponse linéaire. On adoptera donc ici une description phénoménologique du potentiel qui consiste à le supposer localisé dès le départ, sa détermination étant faite en imposant la condition de neutralité du crystal perturbé. La localisation du potentiel se justifie qualitativement grâce à la forte densité d'états des électrons d et est confirmée dans certains cas par des calculs faits dans l'approximation de réponse linéaire.

Les corrélations entre électrons sont complètement négligées dans ce travail et par conséquent l'application des résultats qui suivent à certains alliages (par exemple les alliages à base de Palladium) doit être regardée avec précaution.

EFFETS ASSOCIES AU POTENTIEL D'IMPURETE.

Supposons donc un potentiel $V(\vec{r})$ localisé sur la cellule de l'impureté et considérons son effet sur la structure de bandes définie plus haut. Un tel potentiel produit deux sortes de diffusions. Tout d'abord il y a les processus

intrabandes, où les électrons s et d sont diffusés vers d'autres états s et d respectivement, ces processus étant caractérisés par les éléments de matrice V_{dd} et V_{ss} . D'autre part les éléments de matrice V_{sd} induisent des transitions interbandes, dont il faut distinguer deux types : les processus où l'état initial et l'état final appartiennent à la même bande mais avec un état intermédiaire de l'autre bande ; et les processus où l'état final n'appartient pas à la bande de départ.

Pour une description complète de la perturbation introduite par l'impureté il faut donc en principe résoudre exactement le problème de deux bandes couplées ; cependant étant donné le caractère particulier des bandes s et d, un certain nombre de simplifications peuvent être faites. En effet, la densité d'états d étant nettement plus grande que celle des états s certaines propriétés de ces alliages proviennent presque uniquement de la bande d (cf. 3). Ainsi, l'écran de la charge supplémentaire se fait pratiquement par la bande d, la contribution de la bande s étant assez petite ; les changements de chaleur spécifique électronique et le moment magnétique peuvent être décrits simplement par la diffusion intra-bande d. Par contre, les phénomènes de transport, dus essentiellement aux électrons s font intervenir les transitions s-d induites par l'impureté. En effet, la probabilité de transition d'un électron s vers la bande d est proportionnelle à la densité d'états d, ce qui nous permet de négliger les processus s-s dont la probabilité de transition est proportionnelle à la densité d'états s.

RAPPEL DE LA DIFFUSION DANS LA BANDE d.

Considérons la diffusion, par un potentiel localisé, des électrons d décrits dans l'approximation des liaisons fortes. Ce problème, malgré les simplifications introduites par cette approximation contient encore la difficulté de traiter l'effet de la dégénérescence des états d.

Plusieurs auteurs ont discuté la réponse d'un système dégénéré à une perturbation donnée, en particulier pour les perturbations localisées. L'idée essentielle de ces méthodes consiste à faire intervenir la symétrie du problème en supposant que l'introduction d'une impureté ne détruit pas la symétrie ponctuelle du crystal. Dans un esprit de liaisons fortes et pour des métaux supposés cubiques, introduisons comme base le système de fonctions atomiques $\{i|\lambda\}$

($i = 1, \dots, 5$) centrées sur les sites λ du crystal. On en déduit donc qu'il existe seulement deux éléments de matrice du potentiel $V_{dd}(\Gamma_i) = V(\Gamma_i)$ ($\Gamma_i = \Gamma'_{25}$ et Γ_{12}) et que les éléments de matrice de l'opérateur de Green $G_{ij} = \langle i | 0 | (\epsilon - H_0 + i\delta)^{-1} | j | 0 \rangle$ sont diagonaux. Ces deux remarques permettent la solution exacte de l'équation de Lippmann-Schwinger, $\psi_{dn}^+ = \phi_{dn} + G_0 V \psi_{dn}^+$ où ϕ_{dn} sont les fonctions de Bloch de la n -ème sous bande (cf. 1).

D'autre part ces mêmes considérations permettent d'évaluer les éléments de matrice de l'opérateur $T = V + V G_0 T$. Du fait que la charge déplacée par le potentiel localisé s'écrit en termes d'un déphasage (Blandin, thèse) et que le déphasage est lui-même défini à partir de la matrice T on peut relier cette charge déplacée aux éléments de matrice $V(\Gamma_i)$ et $G_{ii}(\epsilon)$ (cf. 1). Les éléments de matrice $G_{ii}(\epsilon)$ s'obtiennent de la même façon que dans un problème à une bande non dégénérée, à la condition de remplacer la densité d'états totale par l'occupation en énergie des orbitales $\{\Gamma_i\}$, $n(\epsilon, \Gamma_i)$ (cf. 1). Cette quantité est directement calculable à partir des résultats du calcul en liaisons fortes de la structure de bandes du métal pur. On peut donc résumer les résultats qui nous intéressent ici de la façon suivante :

- 1°) La charge déplacée $Z(\epsilon)$ peut s'écrire comme $Z(\epsilon) = \sum_{\Gamma_i} p_{\Gamma_i} \delta(\epsilon, \Gamma_i)$ où $\delta(\epsilon, \Gamma_i)$ est le déphasage associé à la représentation Γ_i et p_{Γ_i} sa multiplicité.

- 2°) Le déphasage $\delta(\epsilon, \Gamma_i)$ a la même forme que dans le cas d'une bande non-dégénérée à condition de remplacer respectivement la densité d'états totale et sa transformée d'Hilbert par $n(\epsilon, \Gamma_i)$ et $F(\epsilon, \Gamma_i)$.

- 3°) L'amplitude de l'orbitale $\{i|0\}$ est encore donnée formellement par la même expression que dans le cas non-dégénéré, avec les mêmes remplacements que pour le déphasage.

- 4°) L'amplitude de diffusion $\langle i\lambda | \psi_{dn}^+ \rangle$ devient infinie pour des énergies $\epsilon > \epsilon_{td}$ (ϵ_{td} étant l'énergie du haut de bande) solutions de $1 - V(\Gamma_i) F(\epsilon, \Gamma_i) = 0$.

On aura donc des états liés de symétrie Γ_i dont l'amplitude à l'origine est donnée par $-F^2(\epsilon, \Gamma_i)/dF/d\epsilon(\epsilon, \Gamma_i)$.

PROPRIETES DU DEPHASAGE $\delta(\epsilon, \Gamma_i)$ ET CHANGEMENT DE DENSITE D'ETATS D

Le changement de la densité d'états $n(\epsilon, \Gamma_i)$ à la limite de faibles concentrations est relié au déphasage par l'expression $\Delta n(\epsilon, \Gamma_i) = \frac{c}{\pi} p_{\Gamma_i} \frac{\partial}{\partial \epsilon} \delta(\epsilon, \Gamma_i)$. L'étude du comportement du déphasage en fonction de l'énergie fournit donc une méthode simple et générale de description de la variation de la densité d'états. Nous allons considérer ici les questions suivantes (cf. 1).

a) - Conditions de validité du modèle de bandes rigides.

Le modèle de bandes rigides consiste à attribuer aux impuretés un simple déplacement de la structure de bandes sans changement de forme. D'après l'expression du déphasage et si les conditions $|V(\Gamma_i) F(\epsilon, \Gamma_i)| \ll 1$ et $|V(\Gamma_i) n(\epsilon, \Gamma_i)| \ll 1$ ($\Gamma_i = \Gamma'_{25}$ et Γ_{12}) sont satisfaites, le changement de densité d'états s'écrit $\sum_i p_{\Gamma_i} n(\epsilon - cV(\Gamma_i), \Gamma_i)$. Donc pour que la structure de bandes se déplace rigidement il faut que $V(\Gamma_i)$ soit faible et indépendant de Γ_i . On s'attend donc, d'après les conditions ci-dessus à avoir des déviations par rapport à ce modèle près de bords de bande pour des fortes perturbations et à l'intérieur de la bande au voisinage des pics de densité d'états.

b) - Effets du comportement de $n(\epsilon, \Gamma_i)$ près des bords de bande.

La densité d'états $n(\epsilon, \Gamma_i)$ au voisinage du haut de bande peut se mettre sous la forme $n(\epsilon, \Gamma_i) \approx \alpha(\epsilon - \epsilon_{top})^x + \beta(\epsilon - \epsilon_{top})^{3/2} \dots$, où x peut prendre les valeurs 0 ou 1/2 et α est donné par $\sum_n | \langle i | \phi(\vec{k}_{top}) \rangle |^2$ (cf. 1). On voit donc que la densité d'états $n(\epsilon, \Gamma_i)$ aura un des deux types de comportement (discontinuité de 1ère espèce ou variation en $(\epsilon - \epsilon_{top})^{1/2}$) seulement si les fonctions atomiques i appartenant à Γ_i sont présentes dans les fonctions de Bloch du bord de bande. Cela nous ramène à considérer trois cas :

- 1°) Effet d'une discontinuité de 1ère espèce.

L'effet essentiel d'une discontinuité de 1ère espèce consiste à introduire une discontinuité logarithmique dans $F(\epsilon, \Gamma_i)$. Dans ce cas $F(\epsilon, \Gamma_i)$ se comporte comme $\log |\epsilon - \epsilon_{top}|$ au voisinage du haut de bande et l'équation $1 - V(\Gamma_i) F(\epsilon, \Gamma_i) = 0$ a toujours une solution pour $\epsilon > \epsilon_{top}$ (état lié d'énergie ϵ) quelle que soit la valeur de $V(\Gamma_i)$. On en déduit que le déphasage prend toujours la valeur $-\pi$ pour $\epsilon = \epsilon_{top}$ et du fait que $dF/d\epsilon(\epsilon_{top}, \Gamma_i) = +\infty$ on déduit que la

dérivée du déphasage est infinie. Si la bande est régulière pour $\epsilon < \epsilon_{\text{top}}$, le déphasage décroît en valeur absolue vers zéro de façon monotone et en conséquence le changement de densité d'états est toujours négatif. Cette diminution de densité d'états signifie physiquement qu'on a enlevé p_r états de la bande pour construire l'état lié.

- 2°) Cas d'une bande parabolique.

Une bande parabolique est caractérisée par une pente positive de $F(\epsilon, \Gamma_i)$ au voisinage de ϵ_{top} et par une pente du déphasage dont la valeur absolue tend vers $+\infty$ quand ϵ tend vers ϵ_{top} . De la pente positive de $F(\epsilon, \Gamma_i)$ on voit que s'il existe une solution de $1 - V(\Gamma_i) F(\epsilon, \Gamma_i) = 0$ à l'intérieur de la bande, cette solution s'accompagne toujours d'une autre à l'énergie $\epsilon > \epsilon_{\text{top}}$ (état lié d'énergie ϵ).

Pour des perturbations suffisamment faibles pour ne pas repousser un état lié, le déphasage part de zéro à ϵ_{top} , passe par un minimum ($|\min \delta(\epsilon, \Gamma_i)| < \pi/2$) et tend vers zéro de façon monotone quand l'énergie s'approche du bas de bande. En conséquence le changement de densité d'états est négatif pour des énergies inférieures à ϵ_m ($\min \delta = \delta(\epsilon_m, \Gamma_i)$) et positif pour $\epsilon_m < \epsilon < \epsilon_{\text{top}}$. Cela veut dire physiquement que la perturbation repousse un certain nombre d'états (toujours inférieur à $p_{\Gamma_i}/2$) d'une large région d'énergie pour les concentrer dans une autre, mais jamais sous forme d'un pic de densité d'états ($\Delta n(\epsilon, \Gamma_i) \rightarrow +\infty$ quand $\epsilon \rightarrow \epsilon_{\text{top}}$).

Si la perturbation devient assez forte pour repousser un état lié de la bande on a un comportement analogue au cas d'une discontinuité de lère espèce. On remarque que malgré le fait d'avoir une solution de $1 - V(\Gamma_i) F(\epsilon, \Gamma_i) = 0$ à l'intérieur de la bande, cette condition nécessaire n'est pas suffisante pour assurer l'existence d'un pic de résonance.

- 3°) Densité d'états de la forme $(\epsilon - \epsilon_{\text{top}})^{n/2}$, $n > 1$.

La différence essentielle par rapport au cas parabolique consiste à avoir les pentes de $F(\epsilon, \Gamma_i)$ et du déphasage respectivement négatives et nulles à ϵ_{top} . De la pente négative de $F(\epsilon, \Gamma_i)$ on déduit l'existence d'un maximum de cette fonction au voisinage de ϵ_{top} et par conséquent la possibilité d'avoir

deux solutions de $1 - V(\Gamma_i) F(\epsilon, \Gamma_i) = 0$ à l'intérieur de la bande. Supposons une perturbation suffisamment faible pour ne pas repousser un état lié mais assez forte pour que les deux solutions existent. Une de ces solutions est assez proche de ϵ_{top} et le déphasage qui part de zéro (avec pente nulle) décroît rapidement pour atteindre des valeurs proches de $-\pi$ et finalement tend vers zéro en passant par $-\pi/2$ à l'énergie correspondante à l'autre solution. Pour les bandes usuelles les deux solutions sont assez éloignées de façon que le déphasage passe assez lentement de valeurs proches de $-\pi$ à zéro. Dans ces conditions le changement de densité d'états présente un pic positif entre ϵ_m et ϵ_{top} ($\min \delta(\epsilon, \Gamma_i) = \delta(\epsilon_m, \Gamma_i)$) et ce pic contient approximativement p_{Γ_i} états. Pour les énergies $\epsilon < \epsilon_m$, le changement de densité d'états est négatif sur une large région d'énergies (donc pas d'effets d'antirésonance). On voit donc qu'un état résonant (état lié virtuel) a été formé et cela est intimement lié au fait d'avoir une pente nulle de la densité d'états à ϵ_{top} . Si la perturbation a repoussé un état lié, le déphasage part de $-\pi$ à ϵ_{top} (avec pente nulle) et tend vers zéro pour des énergies proches du bas de bande. Si la pente de $n(\epsilon, \Gamma_i)$ est nulle au bas de bande, le changement de densité d'états (toujours négatif) présente un minimum. Cela veut dire physiquement que certains états de la bande contribuent plus à la formation de l'état lié.

c) - Effets des pics de densité d'états.

On considère séparément l'effet des pics réguliers de densité d'états et les singularités de Van-Hove.

- 1°) Effets d'un pic régulier de densité d'états.

Considérons un pic de forte densité d'états et de faible largeur $n_p(\epsilon, \Gamma_i)$, superposé à une bande large dont la densité d'états $n_0(\epsilon, \Gamma_i)$ est

telle que $\bar{n}_p \gg \bar{n}_0$, $\bar{n}_0$ et $\bar{n}_p$ étant la densité d'états moyenne de la bande et du pic respectivement. Supposons une perturbation répulsive $V(\Gamma_i)$ telle que $|V(\Gamma_i) F_0(\epsilon, \Gamma_i)| \gg 1$ au voisinage du haut du pic ϵ_{tp} et que les conditions $V(\Gamma_i) n_0(\epsilon, \Gamma_i) \ll 1$ et $V(\Gamma_i) |F_0(\epsilon, \Gamma_i)| \ll 1$ soient satisfaites partout dans la bande $n_0(\epsilon, \Gamma_i)$. Dans ces conditions, des effets de résonance et d'antirésonance sont produits par $V(\Gamma_i)$ au voisinage du pic. Cela est essentiellement lié au fait qu'une des solutions ϵ_{AR} de $1 - V(\Gamma_i) F(\epsilon, \Gamma_i) = 0$ se trouve à l'intérieur du pic et l'autre à une énergie $\epsilon_R > \epsilon_{tp}$.

Dans ces conditions le déphasage $\delta(\epsilon, \Gamma_i)$ prend des valeurs très petites sauf au voisinage du pic pour ces énergies décroissantes $\delta(\epsilon, \Gamma_i)$ passe rapidement de faibles valeurs à des valeurs proches de $-\pi$ dans une région de largeur Δ_p autour de ϵ_R et après augmente très rapidement, tendant vers zéro près du bas du pic ϵ_{bp} . Pour des énergies inférieures à ϵ_{bp} , $\delta(\epsilon, \Gamma_i)$ est plus petit que le déphasage $\delta_0(\epsilon, \Gamma_i)$ correspondant à l'effet de $V(\Gamma_i)$ sur la bande $n_0(\epsilon, \Gamma_i)$ toute seule.

Ce comportement du déphasage entraîne l'existence d'un pic étroit d'antirésonance à l'intérieur de l'intervalle d'énergie correspondant au pic de la matrice ; la largeur de ce pic d'antirésonance est plus petite que la largeur du pic, et la diminution du nombre d'états est voisine de n_p . Par contre, la largeur du pic de résonance est beaucoup plus large que la largeur de $n_p(\epsilon, \Gamma_i)$ ce pic de résonance sera bien marqué seulement si le nombre d'états contenus dans $n_p(\epsilon, \Gamma_i)$ est petit par rapport au nombre total d'états Γ_i dans la bande d.

Le nombre d'états à l'intérieur du pic de résonance n'est proche de n_p que si le déphasage $\delta_0(\epsilon, \Gamma_i)$ est très petit. Cela ne se produit que si la densité d'états $n_0(\epsilon, \Gamma_i)$ est très faible, mais dans ce cas la largeur de l'état résonant est grande. On en déduit donc qu'il ne s'agit pas d'un état lié virtuel dans le sens strict du terme. Physiquement le pic de résonance provient des états du pic de la matrice déplacés en énergie par la perturbation et l'antirésonance correspond à la soustraction de ces états.

- 2°) Singularités de Van-Hove.

Les singularités de Van-Hove sont caractérisées par une discontinuité dans la pente de la densité d'états $n(\epsilon, \Gamma_i)$. La pente de $F(\epsilon, \Gamma_i)$ devient infinie à l'énergie ϵ_{VH} de la singularité, et cela entraîne une pente infinie du déphasage à cette énergie. Le changement de densité d'états présente donc un pic étroit de hauteur infinie. L'hauteur infinie de ce pic n'a pas une signification physique ; cela correspond au fait que la densité d'états $n(\epsilon, c)$ de l'alliage doit varier plus lentement que c , à faibles concentrations, au voisinage d'une singularité de Van-Hove.

DETERMINATION DU POTENTIEL.

La discussion générale de la diffusion dans la bande d a fait intervenir seulement l'hypothèse de localisation du potentiel et la description en liaisons fortes de la bande d . L'esprit de la discussion est toujours le même pour des potentiels décrits dans l'approximation de Hartree ou de Hartree-Fock. Nous abordons maintenant la question de la détermination de ce potentiel, pour une structure de bandes donnée en fonction de la charge d'impureté Z , l'écran étant supposé entièrement fait dans la bande d .

a) - Cas de métaux paramagnétiques.

Dans ce cas, l'approximation de Hartree est supposée valable et la condition d'écran de Friedel $Z(\epsilon_F) = Z = \frac{2}{\pi} \sum_{\Gamma_i} p_{\Gamma_i} \delta(\epsilon_F, \Gamma_i)$ ne fait intervenir que les éléments de matrice $V(\Gamma_i)$ (indépendants du spin), la densité d'états $n(\epsilon_p, \Gamma_i)$ et sa transformée d'Hilbert $F(\epsilon_p, \Gamma_i)$. Même dans le cas où $n(\epsilon_F, \Gamma_i)$ et $F(\epsilon_F, \Gamma_i)$ sont connus par un calcul de bandes, il faut encore faire des hypothèses sur $V(\vec{r})$ pour le déterminer en fonction de Z et de la structure de bandes. En général on suppose que $V(\vec{r})$ a la symétrie sphérique de telle façon que $V(\Gamma_{12}) = V(\Gamma'_{25})$; cette hypothèse faite, on détermine $V(\Gamma)$ de manière univoque en fonction de Z . Cette détermination dans le cas général ne pourrait se faire que par des méthodes numériques, étant donné l'impossibilité d'avoir une expression analytique simple qui relie $V(\Gamma)$ à Z . Cette difficulté provient des différentes multiplicités ($p_{\Gamma'_{25}} \neq p_{\Gamma_{12}}$) des représentations Γ_i . Cependant les calculs existants de $n(\epsilon, \Gamma_i)$ montrent qu'il n'y a pas une très grande

différence entre $n(\epsilon, \Gamma_{12})$ et $n(\epsilon, \Gamma'_{25})$. Cela suggère l'approximation de cinq sous bandes indépendantes ($n(\epsilon, \Gamma_{12}) = n(\epsilon, \Gamma'_{25}) = n(\epsilon)/5$), $n(\epsilon)$ étant la densité d'états totale. Si on emploie cette approximation, on détermine facilement le potentiel en fonction de Z , $n(\epsilon_F)$ et $F(\epsilon_F)$.

b) - Cas des métaux ferromagnétiques.

Le ferromagnétisme de ces métaux est décrit par le modèle de Stoner, le déplacement relatif des deux sous bandes de spin étant donné par $\Delta = n_h J$, n_h étant le moment magnétique par atome (en magnétons de Bohr) et J une énergie d'échange moyenne. L'approximation de Hartree a été employée plusieurs fois, à cause de sa simplicité, pour décrire le potentiel d'impureté dans ces métaux. En effet, dans l'esprit du modèle de Stoner, la seule différence par rapport aux métaux paramagnétiques consiste à introduire dans la condition d'écran les fonctions $n_\sigma(\epsilon, \Gamma_i)$ et $F_\sigma(\epsilon, \Gamma_i)$ (σ décrit le spin), ces fonctions étant déterminées par la relation $G_\downarrow(\epsilon, \Gamma_i) = G_\uparrow(\epsilon + n_h J, \Gamma_i)$ où G désigne F ou n . Dans ces conditions le potentiel se détermine de façon tout à fait analogue au cas des métaux paramagnétiques. Cette approximation cependant, ne permet pas la description dans certains cas (ex : alliages de Fer) des propriétés de ces alliages. Cela vient du fait qu'un potentiel identique pour les deux directions de spin, produit une diffusion différente des états $\uparrow$ et $\downarrow$ et le changement d'énergie d'échange associé à cette diffusion n'est pas consistant avec la description en Hartree-Fock du métal pur.

On introduit donc un potentiel localisé, différent pour chaque direction de spin, dont les éléments de matrice $V_\sigma(\Gamma)$ doivent satisfaire à la fois à la condition d'écran de Friedel et aux équations de Hartree-Fock. La condition d'écran s'écrit dans ce cas $Z_\uparrow = Z_\uparrow(V_\uparrow) + Z_\downarrow(V_\downarrow)$ où $Z_\sigma(V_\sigma) = \frac{1}{\pi} \sum_i p_{\Gamma_i} \delta_\sigma(\epsilon_F, \Gamma_i)$, le déphasage étant défini par V_σ , $n_\sigma(\epsilon_F, \Gamma_i)$ et $F_\sigma(\epsilon_F, \Gamma_i)$. D'autre part, des équations de Hartree-Fock on déduit que la différence $V_\uparrow - V_\downarrow$ doit satisfaire la relation $V_\uparrow - V_\downarrow = -J(\Delta N_\uparrow(V_\uparrow) - \Delta N_\downarrow(V_\downarrow))$ où $\Delta N_\sigma(V_\sigma)$ est le changement du nombre d'occupation des orbitales de l'impureté. Cette équation repose sur l'approximation que l'intégrale d'échange de l'impureté est la même que celle du métal pur. Cette approximation semble raisonnable pour les éléments appartenant à la même série de transition ; son application au cas des alliages de métaux de périodes différentes n'est pas justifiée. La solution simultanée des deux équations de self-consistence est extrêmement complexe à faire en dehors de l'approximation de cinq sous bandes indépendantes. Même dans ce cas la solution doit s'obtenir par des méthodes numériques ; cela est dû au fait que le nombre d'occupation $N_\sigma(V_\sigma)$ s'exprime sous une forme $\int_0^{\epsilon_F} f(V_\sigma, F(\epsilon), n(\epsilon)) d\epsilon$ qui n'admet pas une

expression analytique simple. Cette méthode est analogue à celle employée par Kanamori pour décrire les impuretés de transition dissoutes dans le Ni. La différence essentielle consiste à remplacer la condition de neutralité de l'impureté par la condition d'écran de Friedel ; étant donné les simplifications du modèle cette dernière paraît mieux décrire la situation physique.

APPLICATIONS DE LA DIFFUSION DANS LA BANDE d.

a) - Moment magnétique des impuretés dissoutes dans les métaux ferromagnétiques.

Par la méthode de diffraction de neutrons et les mesures de moment à saturation on a pu déterminer expérimentalement le moment magnétique μ_i des impuretés et la variation du moment magnétique moyen $\bar{\mu}/dc$ dans les alliages ferromagnétiques. Le résultat essentiel de ces mesures est la mise en évidence du changement de signe de ces quantités quand on dissout des éléments éloignés de la matrice dans le tableau périodique. L'étude de ce phénomène peut se faire en termes du modèle proposé pour la diffusion dans la bande d, le potentiel étant traité dans l'approximation de Hartree Fock. Cette étude met en évidence le rôle essentiel de l'apparition d'états liés au dessus de la bande d, dans le changement de signe du moment de l'impureté.

Le nombre d'occupations $N_\sigma(V_\sigma)$ des orbitales de l'impureté, dans le cas d'une sous bande de spin partiellement remplie peut se mettre sous la forme $N_\sigma(V_\sigma) = \frac{\partial}{\partial V_\sigma} \int_0^{\epsilon_F} \delta_\sigma(\epsilon, V_\sigma) d\epsilon$, où $\delta(\epsilon, V_\sigma)$ est le déphasage correspondant à la sous bande σ . On en déduit que si le niveau de Fermi se trouve près du haut de bande, $N_\sigma(V_\sigma)$ décroît rapidement en fonction de V_σ , pour des valeurs du potentiel voisines de celle correspondante à l'apparition d'un état lié au dessus de la sous bande ; cela tient au fait que le déphasage passe de 0 à $-\pi$ en haut de bande quand l'état lié est repoussé. Par contre si le niveau de Fermi se trouve loin du haut de la bande les effets du changement de déphasage se font sentir très faiblement et $N_\sigma(V_\sigma)$ décroît lentement avec V_σ . Dans le cas d'une sous bande de spin complètement pleine, $N_\sigma(V_\sigma)$ est constant et égale à $N_\sigma(0)$ jusqu'à ce qu'un état lié soit repoussé au dessus du niveau de Fermi ; il y a alors une variation discontinue de $N_\sigma(V_\sigma)$ qui passe de la valeur $N_\sigma(0)$ à $N_\sigma(0) - A_\sigma(V_\sigma)$ où $A_\sigma(V_\sigma)$ est l'amplitude sur le site d'impureté de l'état lié de spin σ . Les considérations nous amènent à distinguer deux cas :

- 1°) Cas d'une sous bande de spin complètement pleine (cas du Ni et du Co)

Dans ce cas pour des impuretés telles que le Co, Fe, Mn, l'écran de la charge introduite se fait à l'intérieur de la bande $\uparrow$ et les potentiels nécessaires pour le faire (solutions des deux équations de self-consistence) sont tels que $V_\uparrow$ est inférieur au potentiel critique pour repousser l'état lié $\uparrow$ au dessus du niveau de Fermi. Par contre si on dissout le Cr, V, Ti, la solution self-

consistante $V_{\uparrow}$ est supérieure à la valeur critique et il y a une brusque - 12 -
variation de l'occupation des orbitales $\uparrow$ d'impureté. Cela entraîne un changement
du signe de $V_{\downarrow}$ (positif pour Co, Fe, Mn) et du moment magnétique de l'impureté.
Un raisonnement analogue explique le changement de signe de $d\bar{u}/dc$.

- 2°) Cas de deux sous bandes partiellement remplies (cas du Fer).

Le niveau de Fermi correspondant aux électrons $\uparrow$ se trouve près du
haut de la sous bande $\uparrow$. Quand on dissout le Mn dans le Fer, la solution self-
consistante $V_{\uparrow}$ est inférieure à la valeur critique pour repousser un état lié
et en conséquence $V_{\downarrow}$ étant positif le moment magnétique du Mn est encore positif.
Par contre la dissolution de Cr, V et Ti introduit un excès de charge tel que $V_{\uparrow}$
devient supérieur à la valeur critique, et la présence de l'état lié au dessus
de la bande fait que $V_{\downarrow}$ change rapidement de signe pour une petite variation de $V_{\uparrow}$.
La solution self-consistante $V_{\downarrow}$ devient négative et le moment des impuretés
change donc de signe.

Ce modèle rend compte d'une façon très raisonnable des valeurs observées
expérimentalement aussi bien pour $u_{\downarrow}$ que pour $d\bar{u}/dc$.

b) - Chaleur spécifique électronique.

L'étude expérimentale de la chaleur spécifique électronique de ces
alliages n'est pas très complète dans le cas qui nous intéresse ici. En fait la
plupart des mesures ont été faites à des concentrations assez importantes où
notre modèle ne s'applique pas. Seulement les alliages à base de Fer ont été
étudiés à la limite de faibles concentrations ; les alliages à base de Ni
contiennent en général 10 % d'impuretés. Donc l'application de ce modèle demande
une certaine prudence dans les alliages fortement concentrés.

L'influence d'une discontinuité de 1ère espèce dans la densité d'états
sur $\frac{\Delta n}{\Delta c}$ ($c=0$) a été discutée plus haut. Le cas des alliages de Ni illustrent
qualitativement ce genre de considérations ; en effet on observe que le Co et le
Fe dissous dans le Ni produisent un changement négatif de la chaleur spécifique
électronique. Cela est consistant avec le calcul de bandes de Fletcher où la
discontinuité de la densité d'états en haut de bande apparaît liée au fait que les
surfaces d'énergie constante correspondantes à l'énergie du haut de bande
se réduisent aux diagonales des faces carrées de la zone de Brillouin. Le Mn
et le V dissous dans le Ni produisent par contre un changement positif de
chaleur spécifique. Cela est probablement dû au fait que l'état lié repoussé de
la bande $\uparrow$ et mélangé avec les états s du Ni introduit une forte contribution

positive qui domine l'effet de la bande $\downarrow$.

Une discussion générale du comportement des variations de la chaleur spécifique en fonction de la charge d'impureté Z peut se faire par les méthodes de détermination du potentiel décrites plus haut. Dans l'approximation de 5 sous bandes indépendantes et pour les métaux paramagnétiques on obtient $\frac{\Delta n}{\Delta c}(c=0) = f(Z, \frac{dF}{d\epsilon}(\epsilon_F), R(\epsilon_F))$ où $R^{-1}(\epsilon_F) = \frac{dn}{d\epsilon}(\epsilon_F) / \frac{dF}{d\epsilon}(\epsilon_F)$. Cela se fait en remplaçant le potentiel dans la relation $\frac{\Delta n}{\Delta c}(c=0) = 10/\pi \partial/\partial \epsilon \delta(\epsilon, V_{dd})$ par sa valeur déterminée en termes de Z et de la structure de bandes.

Les changements de signe de la variation de chaleur spécifique sont essentiellement liés au signe de $R(\epsilon_F)$. Par exemple dans le cas des impuretés répulsives ($Z < 0$) on en déduit qu'il y aura un changement de signe pour $Z < -5$ ou pour $0 < Z < -5$ selon que $R(\epsilon_F)$ est positive ou négative. Le cas des métaux ferromagnétiques est traité de façon analogue ; on a simplement à séparer les deux directions de spin pour obtenir $\frac{\Delta n}{\Delta c}(c=0) = \sum_{\sigma} f(2Z_{\sigma}, dF_{\sigma}/d\epsilon(\epsilon_F), R_{\sigma}(\epsilon_F))$, la charge Z_{σ} déplacée dans la sous bande σ , étant calculée à partir des potentiels self-consistents V_{σ} décrits plus haut.

Le cas des alliages à base de Fer est étudié par cette méthode ; expérimentalement on observe que le changement de densité d'états est positif pour le Mn et négatif pour le Cr, V, Ti. Des modèles simples pour la densité d'états du fer pur ont été employés dans ce calcul et le changement de signe de la chaleur spécifique apparaît associé, comme pour le moment magnétique des impuretés à l'apparition d'un état lié au dessus de la sous bande de spin $\uparrow$.

PROPRIETES DE TRANSPORT.

Si on admet selon Mott, que les électrons s sont responsables des phénomènes de transport dans ces alliages, il faut résoudre le problème de deux bandes couplées par le potentiel localisé $V(\vec{r})$. Cela se fait par une généralisation de la méthode de Slater-Koster pour les potentiels localisés, en supposant que les éléments de matrice $\langle \phi_s(\vec{k}) | V(\vec{r}) | \phi_d(\vec{k}') \rangle$ sont indépendants de $\vec{k}$ et $\vec{k}'$. Cette hypothèse permet la solution exacte des équations de Lipman-Schwinger $\psi_i^+ = \phi_i + G_0 V \psi_i^+$ ($i = s, d$) où la diffusion intra-bande $s \rightarrow s$ a été négligée par des arguments présentés dans la discussion des effets du potentiel d'impureté. Le temps de relaxation des électrons s , dans ces conditions, fait intervenir

seulement les éléments de matrice $\langle \phi_i(k') | V(\vec{r}) | \psi_s^+(k) \rangle$, qui s'expriment en fonction des densités d'états n_d et n_s , de la transformée d'Hilbert F_d et des potentiels V_{dd} et V_{sd} .

Le changement total de résistivité dû au mélange s-d induit par l'impureté peut s'exprimer comme la somme de deux contributions : les transitions $s \rightarrow d \rightarrow s$, proportionnelles à $|V_{sd}|^4$ et les transitions $s \rightarrow d$, proportionnelles à $|V_{sd}|^2$. Le dernier type de transition est intimement lié à la largeur finie de la bande d. Si on admet que l'écran de l'impureté est complètement fait à l'intérieur de la bande d, le potentiel V_{dd} peut être déterminé par la règle de Friedel en fonction de Z et de la structure de la bande d. D'autre part les éléments de matrice $|V_{sd}|$ peuvent aussi s'exprimer en termes de Z par la relation $|V_{sd}| = |\alpha_{sd}| V_{dd}(Z)$, où $|\alpha_{sd}|$, le seul paramètre du modèle est défini par le rapport $|\alpha_{sd}| = \int \phi_s^* V(\vec{r}) \phi_d d\vec{r} / \int \phi_d^* V(\vec{r}) \phi_d d\vec{r}$. Dans le cas des métaux paramagnétiques ces considérations permettent d'obtenir des expressions simples de la variation de résistivité résiduelle en fonction de la charge d'écran. Pour les métaux ferromagnétiques on ne considère que la situation où le libre parcours moyen dû aux collisions avec les ondes de spin est petit par rapport à celui correspondant aux collisions avec les impuretés. Dans ce cas le changement de résistivité s'écrit $\Delta\rho = \frac{1}{2} (\Delta\rho_{\uparrow} + \Delta\rho_{\downarrow})$ où $\Delta\rho_{\sigma}$ est le changement de résistivité dû aux électrons σ . Les éléments de matrice V_{dd} maintenant doivent être remplacés par V_{dd}^{σ} et déterminés par la méthode de Hartree Fock, $\Delta\rho_{\sigma}$ s'exprimant maintenant en fonction de Z_{σ} , la charge déplacée dans la bande σ . Le changement de pouvoir thermoélectrique a été calculé à partir de ce modèle et par des arguments analogues s'exprime en fonction de la charge déplacée et de la structure de bandes d.

Ce modèle a pu expliquer qualitativement les résultats expérimentaux disponibles pour les alliages à base de Fer.

PROBLEME DE LA DIFFUSION A PLUSIEURS VOIES.

On introduit le formalisme de la matrice T pour calculer la charge totale déplacée dans un système décrit par plusieurs voies couplées par un potentiel localisé. On construit la matrice $\{T_{\alpha_i, \alpha_j}\}$ où $T_{\alpha_i, \alpha_j} = \langle \alpha_i | T | \alpha_j \rangle = \langle \alpha_i | V | \psi_j^+ \rangle$ en supposant résolu le problème de la diffusion à plusieurs voies. Cette matrice peut être diagonalisée et les déphasages correspondants définis par

$\delta_{\alpha'i} = \arg T_{\alpha'i\alpha'i}^{\sim}$, où $\{T_{\alpha'i\alpha'i}^{\sim}\}$ est la matrice diagonale.

Du fait que la diagonalisation se fait par une transformation unitaire on en déduit que la charge totale déplacée s'écrit $Z = \frac{1}{\pi} \arg \det \{T_{\alpha_i\alpha_j}^{\sim}\}$.

Ces résultats sont appliqués au mélange s-d et à la diffusion avec spin-flip.

Dans le cas du mélange s-d on peut montrer qu'à la limite du potentiel d'impureté infini les deux bandes sont découplées. On en déduit aussi que, pour les énergies supérieures à l'énergie du haut de la bande d, le mélange d'un état lié repoussé de cette bande avec les états s est décrit par la formule d'Anderson pour les états liés virtuels.

C H A P I T R E I

DIFFUSION DANS LA BANDE d : PROPRIETES DU DEPHASAGE ET
CHANGEMENT DE DENSITE D'ETATS

On the use of phase shifts for studying impurity effects in narrow bands, with application to the electronic structure of substitutional alloys of transitional metals.

by

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I - INTRODUCTION.

The purpose of this paper is to review recent advances made in the study of impurity effects in narrow bands. These are assumed to be described in a tight binding (LCAO) approximation, and the use of phase shifts for describing the perturbation is systematically developed.

The bulk of the paper is specifically centred on the electronic structure of substitutional impurities in the d bands of transitional metals, in structures with one atom per cell (i.e. practically FCC and BCC structures); it assumes a perturbation localized on the impurity atom and concentrates on effects related to the density of states. General conditions for the validity of the perturbation or rigid band approximation can then be set up; and the exact nature of the strong deviations from it due to various resonance effects can be defined. We shall show in particular that, strictly speaking, virtual bound d levels can only occur near a band edge, and under very restricted conditions.

As stressed at the end of this paper, the phase shift method can be applied in other cases. Extensions to less localized perturbations and to wide bands are developed. The possible use in the study of interstitial impurities, matrices with more than one atom per cell, phonons or spin wave problems must be mentioned.

The model used for transitional metals is that originally used by Slater to discuss their magnetism [1936] ; the work described here is a direct consequence of the type of analysis of perturbation in narrow bands first made by Koster and Slater [1954] . However, in complex bands deduced from degenerate atomic states such as the d bands of transitional metals, the treatment given here allows a simpler analysis, because it brings out more clearly the symmetry of the problem. The explicit use of phase shifts is of especial interest for a general discussion on the densities of states.

The first part of this paper describes the model used, introduces the general concepts and studies the conditions of validity of the rigid band approximation. A second part is devoted to the strong deviations from this approximation due to resonance effects. A third part reviews some possible extensions of this type of treatment.

II - THE IMPURITY PROBLEM FOR LOCALIZED PERTURBATIONS IN NARROW BANDS.

II.A - THE MODEL.

Having in mind a specific problem of transitional alloys, we shall make in the main part of this paper a number of simplifying assumptions. These will be analyzed and extended in the last part.

a) Band structure.

The band structure for the valence electrons of a transitional metal is made of d and s overlapping bands, on which the following is assumed :

- a) the s-d mixing effects are neglected, in pure metals and in alloys.
- b) the d bands are described by a tight binding method which neglects all overlap integrals except those involving the lattice potential and atomic functions centered on neighbouring sites.

c) spin orbit coupling effects are neglected.

d) the lattice structure is assumed to have one atom per cell, and the d wave functions $\{i\}$ ($i = 1, \dots, 5$) are chosen so that they are basis functions of the irreducible representations Γ of the point group of the lattice. In practice, applications will be made to cubic (FCC or BCC) crystals. The Γ representations are then Γ_{12} or Γ'_{25} .

b) The perturbing potential.

We study highly diluted alloys, when each impurity atom can be considered as acting independently. These impurity atoms are assumed to be substitutional, so that the symmetry of perturbed lattice is that of the (pure) lattice point group.

In the Hartree approximation, the perturbing potential $V_p(r)$ is due to 1) the impurity excess charge and 2) its screening charge, mostly by d electrons. Owing to the screening, V_p has a finite range and, owing to the high density of d states, it is often well localized on the impurity cell. We shall assume for the moment this localization to be complete. Exchange effects, such as the possible apparition of localized magnetic moments, are not considered in this paper.

II.B. - THE T MATRIX AND THE PHASE SHIFT OPERATOR.

From each wave function $|\varphi^{(n)}\rangle$ of the pure metal describing a one-electron state of energy E, one can define an eigenfunction of the perturbed crystal by :

$$|\psi^{(n)}(+)\rangle = T^{(+)}(E) |\varphi^{(n)}\rangle \quad (2.1)$$

where $T^{(+)}(E)$ is the scattering operator defined by

$$T^{(+)}(E) = 1 + \frac{1}{E - H_0 + i\eta} V_p T^{(+)}(E) ; \eta = +0 \quad (2.2.)$$

H_0 is the one electron hamiltonien of the pure metal.

All the properties of the perturbed crystal can be deduced from a knowledge of $T^{(+)}(E)$ and especially the following :

(I) the perturbed wave functions (see (2.1)).

(II) the variation of the number $Z(E)$ of states of energy $E: \leq E$. It is easily shown (Blandin, 1961) that it is related to the phase shift operator $\delta(E)$ by :

$$Z(E) = \frac{1}{\pi} \text{Tr}_E \delta \quad (2.3.)$$

where :

$$\text{tg } \delta(E) = - \pi \delta(E - H_0) V_p K(E) \quad (2.4.)$$

The trace in (2.3) is taken over all the eigenfunctions of energy E and

$$K(E) = T(E) [1 - i \pi \delta(E - H_0) V_p T(E)]^{-1}$$

(III) the variation of the density of states : in the low concentration limit, the change in density of states per unit energy, volume and spin for a concentration c is given by :

$$\delta n(E) = c \frac{dZ(E)}{dE} , \quad (2.5.)$$

All these equations are quite general. The perfect screening of the impurity thus requires exactly :

$$Z(E_F) = Z_0 \quad (2.6.)$$

where E_F is the Fermi level.

II.C. - THE CHOICE OF A REPRESENTATION.

The solution of equation (2.2.) requires the choice of a representation.

In the tight binding approximation, it is natural to chose a representation based on the complete set $|i\lambda\rangle$ of atomic (d) functions $|i\rangle$ centered on the crystalline sites R_λ . This will be called the $\{i\lambda\}$ representation. It neglects the overlap integrals of atomic functions on different sites, and is especially useful if the perturbation potentiel V_p is well localized on the impurity cell. In the spirit of the tight binding approximation, one can then neglect all the matrix elements $\langle i\lambda | V_p | j\mu \rangle$ except these $\langle i0 | V_p | j0 \rangle$ involving the atomic functions on the impurity site.

. For a substitutional impurity in a lattice with one atom per cell, V_p has the symmetry properties of the point group of the lattice. The matrix elements $(i 0 | V_p | j 0)$ then vanish except if the i and j atomic states are identical. The corresponding integral $(i 0 | V_p | i 0) = V_p(\Gamma)$ only depends on the nature of the corresponding class Γ in the irreducible representation of the point group of the lattice. Finally

$$(i \lambda | V_p | j \lambda) = \delta_{ij} \delta_{\lambda\lambda} \delta_{\lambda 0} V(\Gamma) \quad (2.7)$$

In the cubic (FCC or BCC) lattices, there are only two values of $V(\Gamma)$, corresponding to $\Gamma = \Gamma_{12}$ and Γ_{25} .

Introducing the Green functions

$$G_{ij}^{(+)}(E, \lambda \lambda) = (i \lambda | \frac{1}{E - H_0 + i\eta} | j \lambda) \quad (2.8)$$

we have then from (2.2) :

$$(i 0 | T^+(E) | i 0) = [1 - V(\Gamma) G_{ii}^{(+)}(E, 00)]^{-1} \quad (2.9)$$

and the scattering operator is defined in the $\{i \lambda\}$ representation by

$$(i \lambda | T^{(+)}(E) | j \lambda) = \delta_{\lambda\lambda} \delta_{\lambda 0} \delta_{ij} \frac{1}{1 - V(\Gamma_i) G_{ii}^{(+)}(E, 0, 0)} + \quad (2.10)$$

$$+ (1 - \delta_{\lambda 0}) \left\{ (1 - \delta_{\lambda 0}) \delta_{\lambda\lambda} \delta_{ij} + \frac{\delta_{\lambda 0} V(\Gamma_j) G_{ij}^{(+)}(E, \lambda, 0)}{1 - V(\Gamma_j) G_{ij}^{(+)}(E, 0, 0)} \right\}$$

It should be stressed that the use of the $\{i \lambda\}$ representation would be strictly equivalent to that of the Wannier representation first developed by Koster and Slater (1954), if the narrow band considered derived from non degenerate atomic orbitals (Wolff, 1961), Clogston, (1962); Seeger, (1962); Goodings (1964). But, for narrow bands derived from degenerate atomic orbitals such as the d band of transitional metals, the use of the Wannier representation leads to much more complex equations than the $\{i \lambda\}$ representation. The physical reason is that each (d) subband does not, in general, possess, as a whole, the symmetry properties of the lattice, which therefore do not come out clearly out of the equations. As a result, no simplification comparable to equation (2.7) occur in the Wannier representation : the matrix elements of V_p between Wannier functions of different d subbands are usually different from zero ; the Wannier functions of one subband are not well localized on an atomic cell, so that

important matrix elements of V_p can involve Wannier functions centered on other sites than the impurity one, even when V_p is itself well localized on the impurity site (Gautier et al 1965 a).

II.D. - MAIN RESULTS IN THE $\{i\lambda\}$ REPRESENTATION.

From the knowledge of $T^{(+)}(E)$, equation (2.10), we can formally deduce the wave functions and the displaced charge. The corresponding changes in density of states will be then discussed in full.

1)- Wave functions.

The perturbed function $|\psi^{(n)(+)}(k)\rangle$ related by (2.1) to the Bloch function $|\varphi^{(n)}(k)\rangle$ of the n^{th} subband with wave vector k is given by :

$$(i\lambda|\psi^{(n)(+)}(k)\rangle = \sum_j \langle j|\varphi^{(n)}(k)\rangle \left[\delta_{ij} e^{i k \cdot R_j} - \frac{V(R_j) G_{ij}^{(+)}(E, \lambda, 0)}{1 - V(R_j) G_{ij}^{(+)}(E, 0, 0)} \right] \quad (2.11)$$

Note that there is a mixing of the various i components of the wave functions of the pure matrix : this is because each Bloch function is itself a mixing of orbitals of various symmetries. It will be seen below that the scattering amplitude in (2.11) is related to the phase shifts.

2)- Displaced charge $Z(E)$.

From (2.3), the charge $Z(E)$ is given by

$$Z(E) = \frac{1}{\pi} \sum_{\Gamma} p \delta(E, \Gamma) \quad (2.12)$$

where p is the dimension of the irreducible representation Γ . Thus, for cubic lattices, $p = 2$ for Γ_{12} and 3 for Γ'_{25} . From (2.4) and (2.9), we then have

$$\mathcal{G}(E, \Gamma_i) = t g^{-1} \left[- \frac{V(\Gamma_i) n(E, \Gamma_i)}{1 - V(\Gamma_i) F(E, \Gamma_i)} \right] \quad (2.13)$$

where $n(E, \Gamma_i)$ and $F(E, \Gamma_i)$ are respectively the imaginary and real parts of $G_{ii}^{+}(E, 0)$

From the definition (2.8), $n(E, \Gamma_i)$ is the density of occupation of one of the $\{i\}$ orbitals of the Γ_i class at energy E and per unit of energy, spin and atomic volume :

$$n(E, \Gamma_i) = (i|\mathcal{G}(E - H_0)|i) \quad (2.14)$$

It is given, in the Bloch representation, by

$$n(E, \Gamma_i) = \frac{\Omega}{(2\pi)^3} \sum_n \int_{S_n(E)} \frac{dS_n}{|\nabla_{\mathbf{k}} E_n|} |(i|\varphi^{(n)}(\mathbf{k})|)^2 \quad (2.15)$$

Ω is the atomic volume, and the integration is taken over the surfaces $S_n(E)$ of constant energy $E = E_n(\mathbf{k})$. The orthonormalization of the Bloch functions $\varphi^{(n)}(\mathbf{k})$ leads to the sum rules :

$$\int_{-\infty}^{+\infty} n(E, \Gamma_i) dE = 1 \quad (2.16)$$

$$\sum_i p n(E, \Gamma_i) = n(E) \quad (2.17)$$

where $n(E)$ is the ordinary density of states per unit energy, spin and atomic volume of the unperturbed matrix.

From equation (2.2), the function $F(E, \Gamma_i)$ is similarly the Hilbert transform of $n(E, \Gamma_i)$:

$$F(E, \Gamma_i) = P \int \frac{n(E', \Gamma_i) dE'}{E - E'} \quad (2.18)$$

P is the Cauchy principal part.

We can note from equations (2.12) and (2.15) that completely filled or empty subbands do not contribute directly to the total displaced charge, i.e. to the screening, although their presence affects contribution of the partially filled subbands through their contribution to $F(E, \Gamma_i)$. They also contribute directly to the spatial variation of the displaced charge through their action on the wave functions (eq.2.11) and eventually through the occurrence of bound states extracted from them.

III - CHANGE IN THE DENSITY OF STATES DUE TO ALLOYING.

III.A - GENERAL CONSIDERATIONS.

This important aspect of the electronic perturbation due to impurities can be fairly directly related to changes in measurable properties (e.g. electronic specific heat, paramagnetism, Knight shift). These experimental results have been extensively discussed using either a 'rigid band model' which assumes that the extra electrons of the impurities fill the d band of the matrix without otherwise changing its form (Mott and Jones 1936), or the concept of 'virtual bound state', which assumes that the d states of the impurity poorly mixes with the d band of the matrix (Clogston 1962).

In this chapter, we want to discuss the conditions of validity of the rigid band model and the nature of the strong deviations from that model that can be due to resonant effects, leading eventually to the formation of virtual bound states. We shall show how the use of the phase shift concept helps to obtain fairly general results without having to work out numerical results on a specific model.

In the low concentration limit, the change in the density of states due to alloying is directly related to the energy variation of the displaced charge $Z(E)$, thus of the phase shifts $\delta(E, \Gamma)$. Equation (2.5) gives :

$$\delta n(E) = c \frac{1}{\pi} \sum_{\Gamma} p \frac{d\delta(E, \Gamma)}{dE} \quad (3.1)$$

The contributions $n(E, \Gamma_i)$ of the various symmetry classes Γ are therefore additive, and can be discussed separately, using (2.13) for computing the phase shifts $\delta(E, \Gamma)$.

We can assume $n(E, \Gamma)$ and $\frac{dn(E, \Gamma)}{dE}$ to be continuous in E nearly everywhere in the band. Then the following properties follow, which will be useful in the discussion :

P.1. $F(E, \Gamma)$ and $\frac{dF(E, \Gamma)}{dE}$ are continuous in the energy ranges of continuity of $n(E, \Gamma)$ and $\frac{dn(E, \Gamma)}{dE}$ respectively.

P.2. When $n(E, \Gamma)$ has a first type of discontinuity for $E = E_1$, i.e. $n(E_1 + 0) \neq n(E_1 - 0)$, $F(E, \Gamma)$ has a logarithmic infinity for $E = E_1$. The same applies for dn/dE and dF/dE .

P.3. For $E \geq E_t$, energy at the top of the band, $F(E, \Gamma)$ is positive and decreases with increasing energy E ; in the same way, for $E \leq E_b$, energy at the bottom of the band, $F(E, \Gamma)$ is negative and decreases with increasing energy. Also, from P.1., there is necessarily an energy E_0 for which $F(E_0, \Gamma) = 0$. Finally $F(E, \Gamma)$ has generally a relative maximum of amplitude near the band edges.

P.4. When the density of states $n(E, \Gamma)$ is zero at a band edge, we have for that energy ($E = E_b$ or E_t) :

$$\frac{d\delta(E, \Gamma)}{dE} = - \frac{\pi V(\Gamma)}{1 - V(\Gamma) F(E, \Gamma)} \frac{dn(E, \Gamma)}{dE} \quad (3.2)$$

Finally, for a solution E_i of the equation

$$1 - V(\Gamma) F(E, \Gamma) = 0 \quad (3.3)$$

we have

$$\frac{d\delta(E_i, \Gamma)}{dE} = - \frac{dF(E_i, \Gamma)/dE}{n(E_i, \Gamma)} \quad (3.4)$$

P.5. Expanding equation (2.15) in powers of $E_t - E$ gives :

$$n(E, \Gamma) = \sum_n |(i | \psi^{(n)}(k_{tn}) \rangle|^2 n^{(n)}(E) + \frac{\Omega}{2(2\pi)^3} \int_{S_n(E)} \frac{dS_n}{|\nabla_{\mathbf{k}} E|} (k - k_{tn}) \cdot \nabla_{\mathbf{k}} \nabla_{\mathbf{k}_{tn}} |(i | \psi^{(n)}(k) \rangle|^2 (k - k_{tn}) \quad (3.5)$$

The vectors k_{tn} are at the top of the band structure, and the centrosymmetry of the surfaces S_n of constant energy has been used. From a theorem by Van Hove (1953), the first term is of order $(E_t - E)^0$ or $(E_t - E)^{1/2}$, the second of order $(E_t - E)^{3/2}$. The behaviour of $n(E, \Gamma)$ near a band edge therefore depends on whether the integrals $(i | \psi^{(n)}(k_{tn}) \rangle$ corresponding to all the atomic orbitals $|i\rangle$ belonging to Γ vanish or not.

For instance, in FCC nickel or cobalt, the top of the d band occurs at the X points in k -space, and the wave functions at the top of the band have only Γ_{25} components (Fletcher, 1952). In BCC iron, the top of the band seems to be at the H points, and only Γ_{12} components occur (Abate and al, 1965).

III.B. - CONDITIONS OF VALIDITY OF THE RIGID BAND MODEL.

To first order in the perturbation $V(\Gamma)$, equation (2.13) gives :

$$\delta(E, \Gamma) = - \pi V(\Gamma) n(E, \Gamma) + O_2(V) \quad (3.6)$$

The contribution of the Γ class to the change in density of states is thus

$$\delta n(E, \Gamma) = - V(\Gamma) \frac{dn(E, \Gamma)}{dE} + O_2(V) \quad (3.7)$$

The perturbed density of states $n(E, c)$ for a concentration c of impurity can thus be written

$$\sum_{\Gamma} p n(E - c V(\Gamma), \Gamma) \quad (3.8)$$

Thus, to first order in $V(\Gamma)$ the contribution of the Γ class to the density of states is thus rigidly shifted by an amount $cV(\Gamma)$, without change of form. If the $V(\Gamma)$ are equal for all the classes, the whole density of states $n(E)$ is shifted by $c V(\Gamma)$ without change in form*.

* The same result can of course be deduced from the change of energy, to first order in V , of a Bloch state : $E^{(n)}(k) = \langle \psi^{(n)}(k) | V_p | \psi^{(n)}(k) \rangle = \sum_i V(\Gamma) |\langle \psi^{(n)}(k) | i \rangle|^2$

is independent of n and k if all the $V(\Gamma)$ are equal.

The rigid band model is thus valid in the Born (first order) approximation, but only if crystalline field effects are neglected. In cubic lattices, the two $V(\Gamma)$'s would strictly be equal if V_p had spherical symmetry. Their difference is usually small compared with the band width, and this explains the fair success of the rigid band model for substitutional impurities with small Z's, thus near to the matrix in the periodic table.

We wish now to discuss possible strong deviations from the Born approximation required by the rigid band model. These will occur whenever either of the two following conditions is not fulfilled :

$$|V(\Gamma) - F(E, \Gamma)| \ll 1 \quad (3.9)$$

or

$$|V(\Gamma) - n(E, \Gamma)| \ll 1 \quad (3.10)$$

Deviations are, of course, expected for large perturbations $V(\Gamma)$; for a given perturbation, they are expected mostly in the following zones of energy :

- (I) outside the band (bound states).
- (II) within the band, near the band edges (see P.3. and (3.9)).
- (III) near peaks of the density of states : $n(E, \Gamma)$ or $F(E, \Gamma)$ take then large values (cf (3.9) or (3.10)).

III.C - THE OCCURENCE OF BOUND STATES.

When $V(\Gamma) \gg [F(E_t, \Gamma)]^{-1}$, the scattering amplitudes of (2.11) are infinite for the energy $E_s \gg E_t$ of a bound state, solution of

$$F(E_s, \Gamma) = 1/V(\Gamma) \quad (3.11)$$

From the monotonic variation of $F(E, \Gamma)$ outside the band, there is only one (possibly degenerate) solution for each class Γ at a given value of $V(\Gamma)$. Thus in the cubic lattices, two degenerate Γ_{12} and three degenerate Γ_{25} bound states are separately extracted from the d band. Similar conclusion would apply for a strong enough attractive perturbation and bound states below the band. The bound state transforming like the orbital $|i\rangle$ has an amplitude on the central cell which is easily obtained

$$|(i | \Psi_{i(E_s)})|^2 = - F(E_s, \Gamma)^2 / \frac{dF(E_s, \Gamma)}{dE} \quad (3.12)$$

We can note that the extension of the bound states, when just extracted from a band, are very different depending on the way $n(E, \Gamma)$ varies near the band edge.

Thus, when $n(E, \Gamma) \propto (E_t - E)^{\frac{1}{2}}$, the bound state has an infinite extension when it emerges from the band. When $n(E, \Gamma) \propto (E_t - E)^{3/2}$, it emerges with a finite extension.

III. D - THE OCCURENCE OF VIRTUAL BOUND STATES NEAR A BAND EDGE.

As for free particles, a virtual bound state will be defined as a positive peak produced in the density of states by the perturbation. To be a proper virtual bound state, this peak must be narrow compared with the features of the density of states of the matrix ; its area must also correspond, at least roughly, to the number of bound states that could occur in the same class . In other words, $\delta(E, \Gamma)$ must vary by an amount near to $\mathcal{N}$ over a narrow range of energy.

The possible occurence of such virtual bound states of a given class near a band edge is shown to depend on the behaviour of the corresponding density of states $n(E, \Gamma)$ near that edge. We shall show that a repulsive perturbation can only produce a virtual bound state near the top of the band if the wave functions at the top of the band do not contain atomic orbitals of the same class. A somilar result can be obtained for attractive perturbations and the botton of the band.

We examine the deviations from the rigid band model produced by a repulsive potential V_p near the top E_t of the d band. V_p is thus too strong for conditions (3.9) or (3.10) to apply ; but we assume it is not strong enough to extract a bound state. Thus from (3.11), $V(\Gamma) < F(E_t, \Gamma)^{-1}$. From P.1., this requires $n(E_t - 0, \Gamma) = 0$: virtual bound states of the Γ class cannot occur near an edge with a finite corresponding density of states. From P.5., the only cases to discuss are therefore those where $n(E, \Gamma) \propto (E_t - E)^n$, with $n = \frac{1}{2}$ or $\frac{3}{2}$. $F(E, \Gamma)$ is then finite and continuous at $E = E_t$. If it has a negative slope just below E_t , the equation (3.3) has at least two solutions E_i ($i = 1$ and 2) within the band : $E_1 \leq E_2 < E_t$. The scattering cross section wich appears in (2.11) has a finite maximum for $E = E_2$. We shall show however that this 'resonance' condition is not sufficient to produce a proper virtual bound states, contrary to what has been sometimes stated (Wolff, 1961 ; Clogston, 1962).

a) $n(E, \Gamma) \propto (E_t - E)^{\frac{1}{2}}$ (i.e. the Bloch states at the band edge have Γ components).

The phase shift $\delta(E, \Gamma)$ decreases from 0 at the band edge with decreasing energies, with an initial infinite slope (P.4., cf Fig.1).

When $n(E, \Gamma)$ is less than its parabolic development over all the d band, it can easily be shown that $F(E, \Gamma)$ has a positive slope just below E_t (Gautier et al, 1965 b). $\delta(E, \Gamma)$ is then always less than $\frac{\pi}{2}$ (fig.1), and no resonance occurs. This general case is similar to the behaviour of the 's' phase shift in the scattering of f particles by a spherical potential.

If $n(E, \Gamma)$ is greater than its parabolic development, $F(E, \Gamma)$ can have a negative slope just below E_t ; in that case, it has necessarily a maximum within the

band width. Equation (3.3) has then at least two solutions E_1 and E_2 , between which $|\delta(E, \rho)| > \frac{\pi}{2}$. However the change in density of states due to the impurity, proportional to $d\delta/dE$, decreases continuously from $+\infty$ to negative values when the energy E decreases from E_t to E ; there is usually no maximum of $d\delta/dE$ in this range of energy. Figure 2 shows, as an example, the various functions of interest for a localized potential acting on a non degenerate band in the simple cubic structure. In fact a strong peak in the density of states near E_t generally required to produce such a maximum. The corresponding resonant state will be studied below III.E; it is not a proper virtual bound state.

In conclusion, whatever the form of $F(E, \rho)$ near the top of the band, no virtual bound state can be produced if $n(E, \rho) = \alpha (E_t - E)^{\frac{1}{2}}$.

b) $n(E, \rho) = \alpha (E_t - E)^{3/2}$ (i.e. the Bloch states at the band edge have no Γ component).

From the continuity of $dn(E, \rho)/dE$ at the band edge and from P.2., one deduces that $dF(E, \rho)/dE$ is continuous at the band edge, and therefore negative. Also, from P.4., the phase shift has a vanishing slope at the band edge. It is then easily shown that a virtual bound state necessarily occurs near the band edge when the perturbation is not quite strong enough to produce the corresponding bound state. For, when $V(\rho) \rightarrow [F(E_t, \rho)]^{-1}$, the phase shift $|\delta(E, \rho)|$ which starts from E_t with zero slope, crosses the value $\frac{\pi}{2}$ and reaches values near to π in an energy range that tends towards E_t (Fig.3). The variation is similar to that of the 'p' phase shift for free electrons.

The virtual bound state produced has the following characteristics :

- The top of the peak in its density of states occurs at an energy E_c defined by $d^2\delta/dE_c^2 = 0$. It is usually distinct from the resonant energy E_2 such that $\delta = \pi/2$; but both energies tend towards E_t when $V(\rho) \rightarrow [F(E_t, \rho)]^{-1}$.

- Its width is of the order of $-\pi/(d\delta/dE_2) = -\pi n/(dF/dE_2)$ and it decreases as $(E_t - E_2)^{3/2}$ when the state tends towards the edge.

- The number of supplementary states per impurity atom, deduced from the area of the peak tends towards the number of atomic states of the Γ class when $E_2 \rightarrow E_t$.

- These states are subtracted from an energy region centered around the other solution E_1 of equation (3.3). But it is usually subtracted from a large part of the band, so that there is no marked antiresonant peak in the density of states.

III.E - RESONANT AND ANTIRESONANT EFFECTS NEAR TO A PEAK OF DENSITY OF STATES.

We shall now analyse shortly the possible effects of features of the density of states that occur within the band, away from the edges. We shall distinguish the possibilities of strong regular peaks of density and of Van Hove anomalies. We

shall show that the resonant effects possible in these cases are not proper virtual bound states.

Let us assume that a ~~high~~ and sharp peak p of density $n_p(E, \Gamma)$, is superimposed on a regular density of states $n_0(E, \Gamma)$.

For very small $V(\Gamma)$'s, when the rigid band model applies, the peak p produces in the same energy range a peak in the change of density of states due to alloying. The total number of states per impurity atom is proportional to $V(\Gamma)$ and to the total number of states in peak p .

We next consider $V(\Gamma)$ large enough for the condition $\sqrt{V(\Gamma)} \frac{F_p(E, \Gamma)}{F_0(E, \Gamma)} \gg 1$ to apply near the energy E_t^p at the top of the peak p but with still $\sqrt{V(\Gamma)} \frac{F_p(E, \Gamma)}{F_0(E, \Gamma)} \ll 1$ over the whole range of energy of the band ($E_b < E < E_t$).

The corresponding variation of $\delta(E, \Gamma)$ is shown figure 4. From (a), it has very small values except near the peak. From (b), the condition (3.3) is fulfilled for an energy $E_R > E_t^p$ as well as for an energy E_{AR} which falls within the peak. For decreasing energies, the phase shift $\delta(E, \Gamma)$ thus decreases sharply from small values to values near to $-\pi$ around E_R , then increases sharply from near to $-\pi$ to near to zero around E_{AR} . For energies below the peak, $\delta(E, \Gamma)$ is lower than the value $\delta_0(E, \Gamma)$ deduces from the action of $V(\Gamma)$ on $n_0(E, \Gamma)$ only.

The change in density of states due to the impurities has thus the following characteristic features in this special case (Fig. 4) :

- a sharp antiresonant peak within the peak p of the matrix. The width $\Delta_{AR} = E_t^p - E_{AR}$ of this peak is less than the width of the peak p and the high energy side of it for repulsive perturbations. The number of states per impurity atom contained in this antiresonant peak is nearly equal to the degeneracy of the Γ class in the limit of a large and narrow peak.

- a resonant peak in the energy range above the peak ($E_t^p < E < E_t^p + \Delta_R$). Its width Δ_R is much larger than that of the peak p . It can be shown (Gautier et al, 1965 b) that Δ_R increases with the number of states contained in peak p , so that the resonance peak is well marked only if this is a small fraction of the total number of Γ states in the d band. The number of states per impurity atom contained in the resonant peak is only near to the degeneracy of the Γ class if the phase shift $\delta_0(E, \Gamma)$ due to the broad part of the band is very small. This requires that $n_0(E)$ is small, in which case, as we have seen, the resonant peak is broad.

- an increase in density below E_{AR} , with a large width, of order Δ_R . The corresponding number of states must of course be just equal to the difference between the antiresonant and the resonant peak.

These results are preserved qualitatively for still larger perturbations, such that $V(r) / F_0(E, r) \gg 1$, but with a smaller resonant peak and a more complex variation of the phase shift.

It can be said in a qualitative way that the resonant state described in this section is due to the d states of the matrix originally in the peak p and shifted in energy by the perturbation ; in the same way, the antiresonant state describes the subtraction of those states from peak p. We have seen however that the resonant state is only well defined when its area is small. It should therefore not be confused with proper a virtual bound state.

III. F - Van Hove SINGULARITIES.

Van Hove singularities (Van Hove, 1953) are expected in all bands, and in particular in the d band of transitional metals. Indeed most of the peaks in their density of states are probably non regular and correspond to such singularities (cf Wohlfarth and Cornwell, 1961).

At the energy E_s of such a singularity, the break in $\frac{dn(E, r)}{dE}$ produces an infinity in $\frac{dn(E, r)}{dE}$ (cf P.2). The phase shift $\phi(E, r)$ has thus an infinite slope; the change in density due to alloying has a very sharp peak with an infinite height.

Two points should be stressed :

(a) - These phase shift singularities are localized in a narrow range of energy. As an example, the singularities related to one non degenerate band in the simple cubic structure are shown figure 2 .

- The infinity in the change $n(E, c) - n(E, 0)$ of density of states has no physical reality. It only means that the density of states $n(E, c)$ of the alloy varies more slowly than the concentration c near the Van Hove singularity $E = E_s$. A similar effect has been discussed by Lifschitz (1964).

References

- J.C. Slater, Phys. Rev., 49, 537 (1936).
- G.F. Koster and J.C. Slater, Phys. Rev, 95, 1167 (1954).
- P.A. Wolff, Phys. Rev., 124, 1030 (1961).
- A.M. Clogston, Phys. Rev., 126, 439 (1962).
- A. Seeger and H. Staatz, Phys. Stat. Sol. 2, 857 (1962).
- D.A. Goodings and B. Moser, 136, A1093 (1964).
- F. Gautier and P. Lenglard, Phys. Rev., 139, A705 (1965 a).
- A. Blandin (Thesis Paris 1961).
- N. Nott and Jones, The Theory of properties of metals and alloys (1936).
- G.C. Fletcher, Proc. Phys. Soc. London, 65, 192 (1952)
- E. Abate and M. Asdente, Phys. Rev. 140, A 1303 (1965).
- F. Gautier and A.A. Gomès (To be published 1965 b)
- Van Hove, Phys. Rev., 89, 1189 (1953).
- E.P. Wohlfarth and T.F. Cornwell, Phys. Rev. Let. 7, 342 (1961)
- I.M. Lifshitz, Adv. Phys. 13, 483 (1964).
- J. Kanamori, J. App. Phys. 36, 929 (1965).
- J. Callaway, J. Math. Phys. 5, 783 (1964).
- S. Olszewsky (Thesis Paris 1962).
- A.M. Clogston, Phys. Rev, 136, A 1417 (1964)
- Des Cloizeaux 1965, Phys. Rev. 135, A685 (1964) - Phys. Rev. 135, A698 (1964).
- J. Friedel, Adv. in Physics, 3, 446 (1954)

Figure Captions

Fig.1 - $F(E)$, $\hat{f}(E)$ and $\frac{\partial n(E,0)}{\partial c}$ for $n(E)$ less than its parabolic development (schematic)

Fig.1bis- $F(E)$, $\hat{f}(E)$ and $\frac{\partial n(E,0)}{\partial c}$ for $n(E)$ greater " " " "

Fig. 2- Phase shift curves for a non-degenerate band in the simple cubic structure.

Fig. 3- $F(E)$, $\hat{f}(E)$ and $\frac{\partial n(E,0)}{\partial c}$ for a band such that $\frac{dn(E_t)}{dE} = 0$ (schematic) •

Fig. 4- Effect of a sharp peak in $\hat{f}(E)$ and $\frac{\partial n(E,0)}{\partial c}$ (schematic).

Fig. 5.a. and 5.b. - Effect of a Van Hove singularity (schematic).

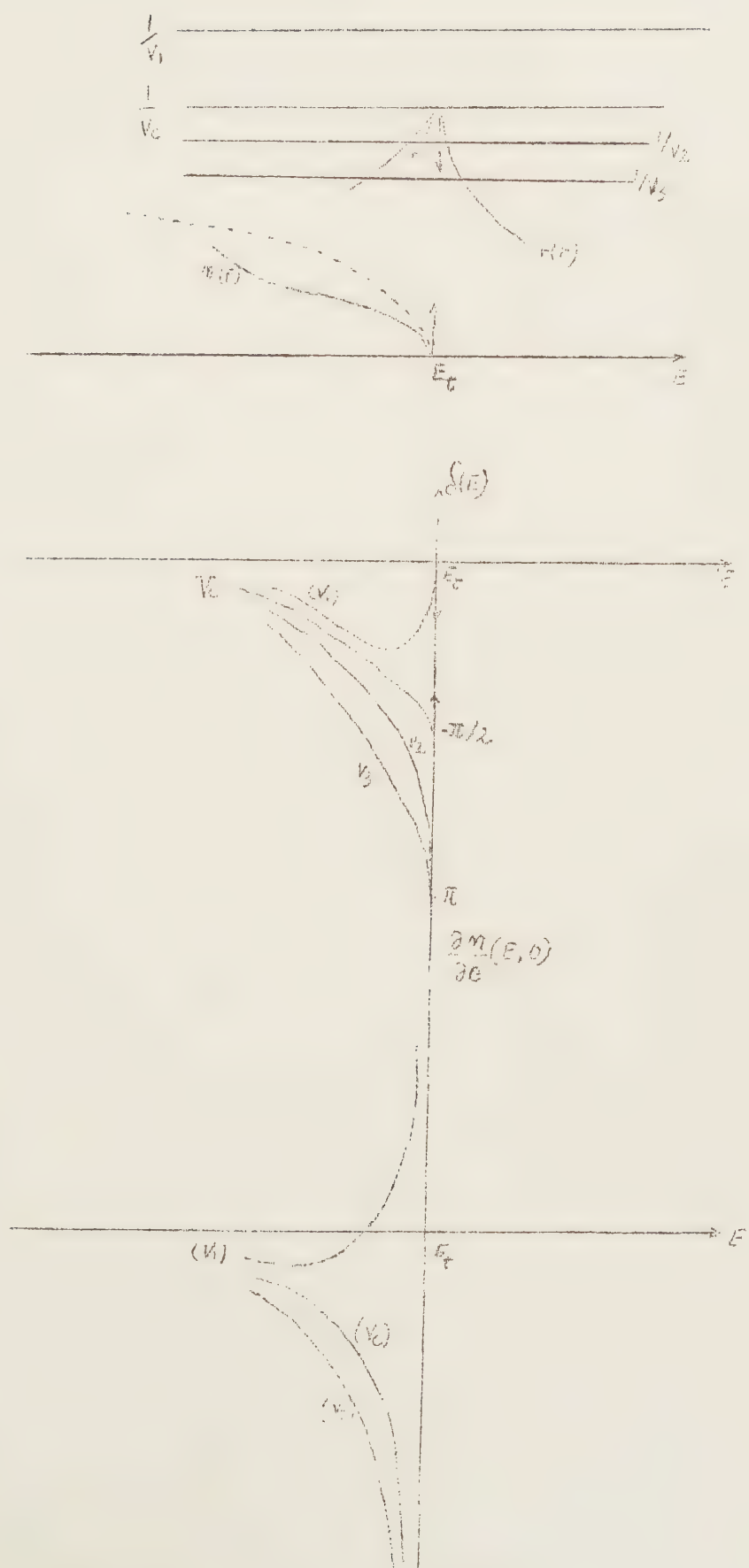


Figure 1

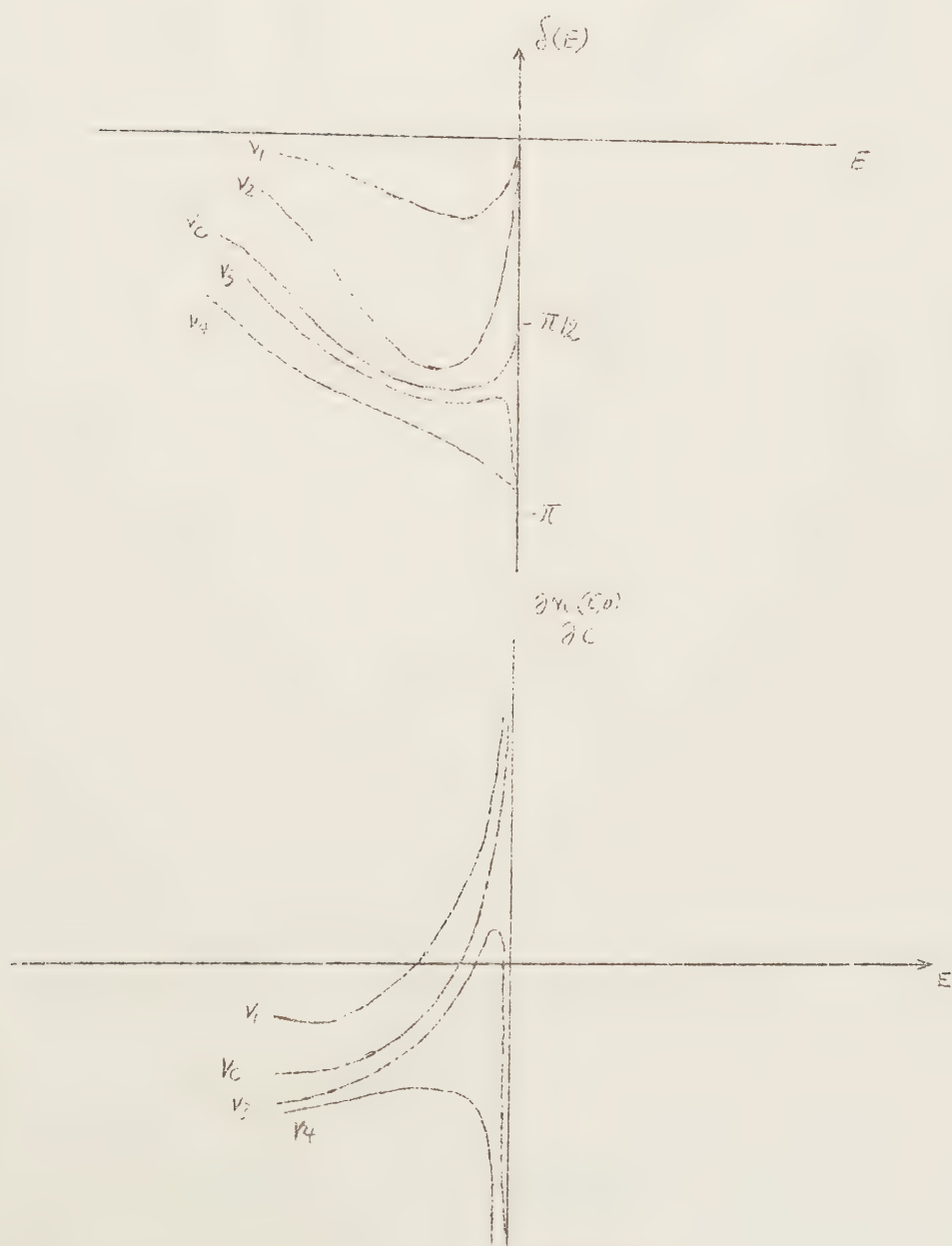
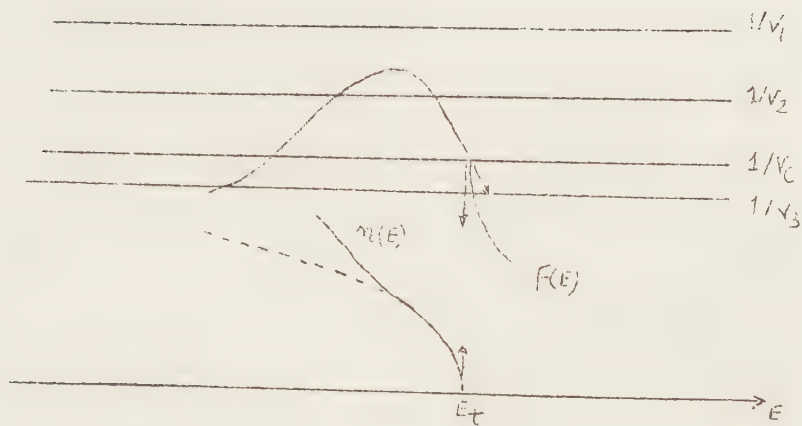


Figure 1 bis

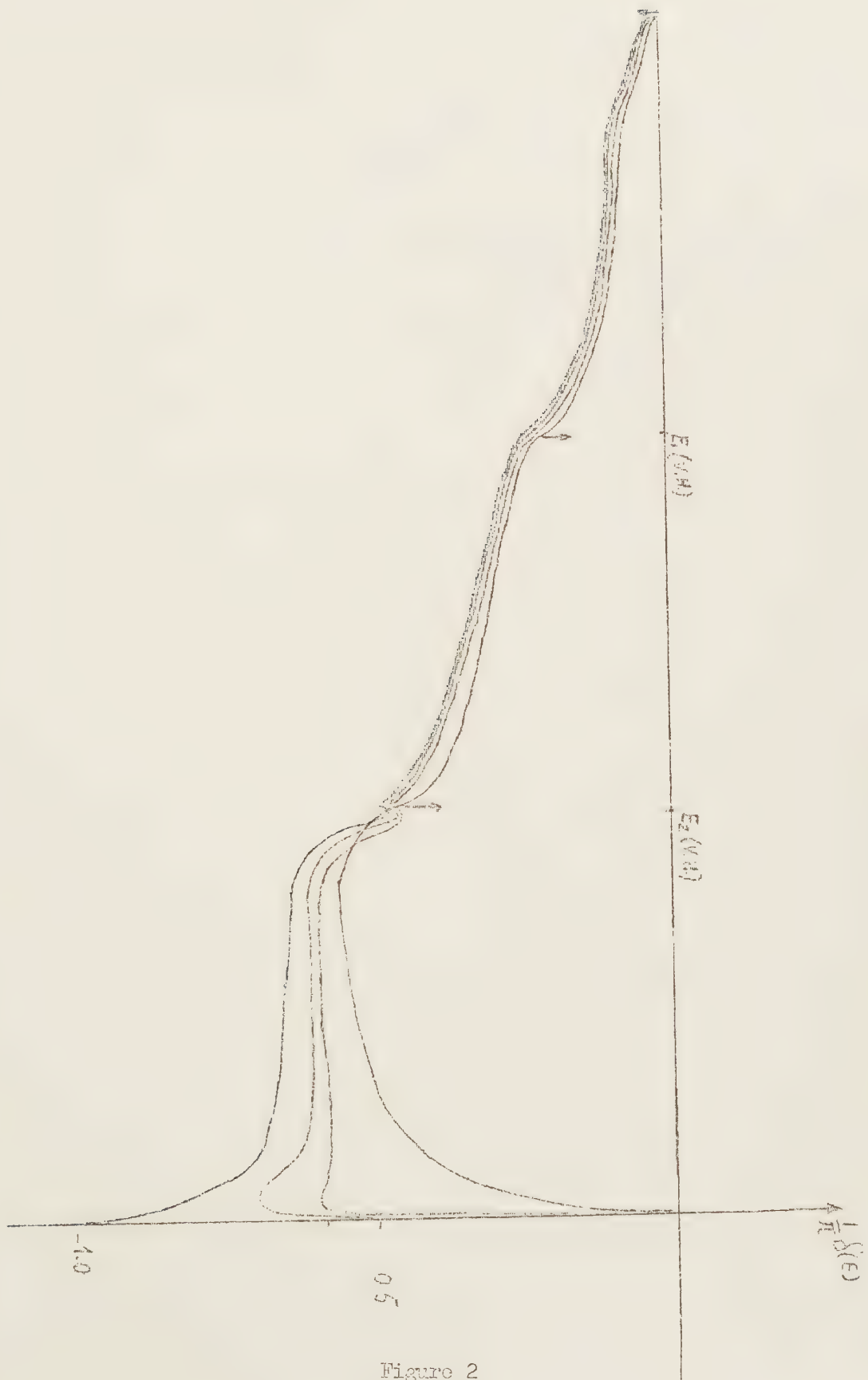


Figure 2

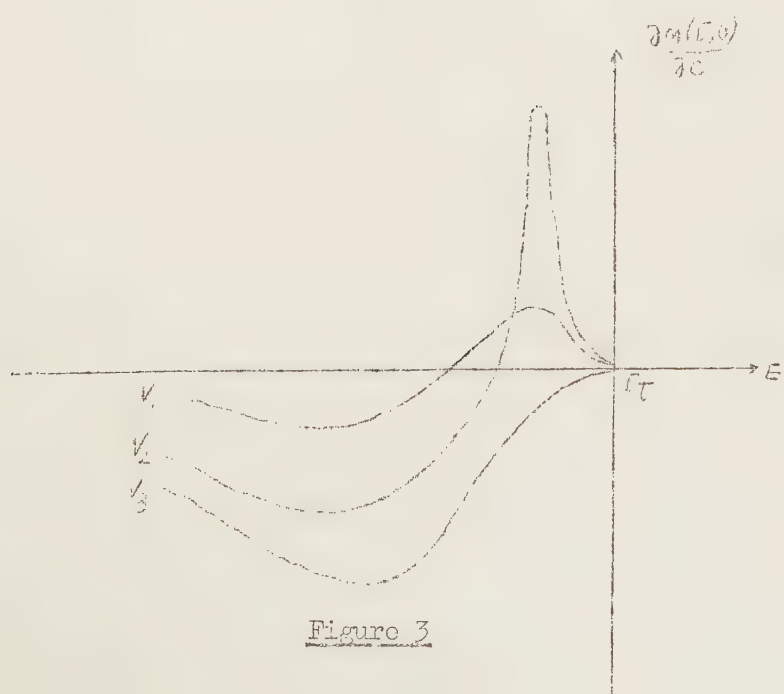
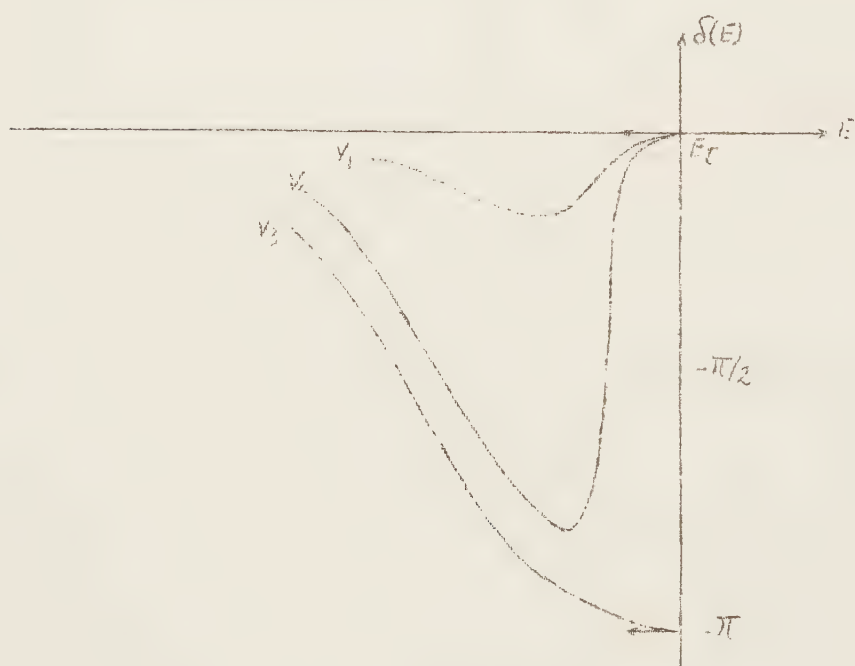
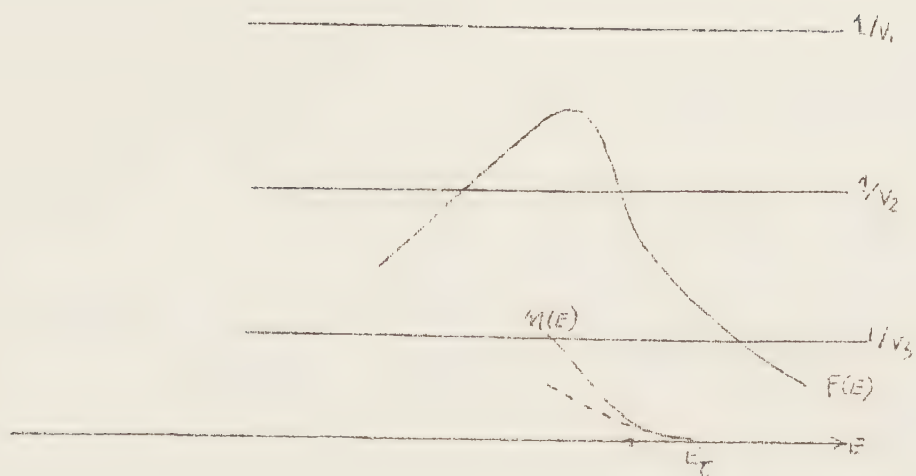
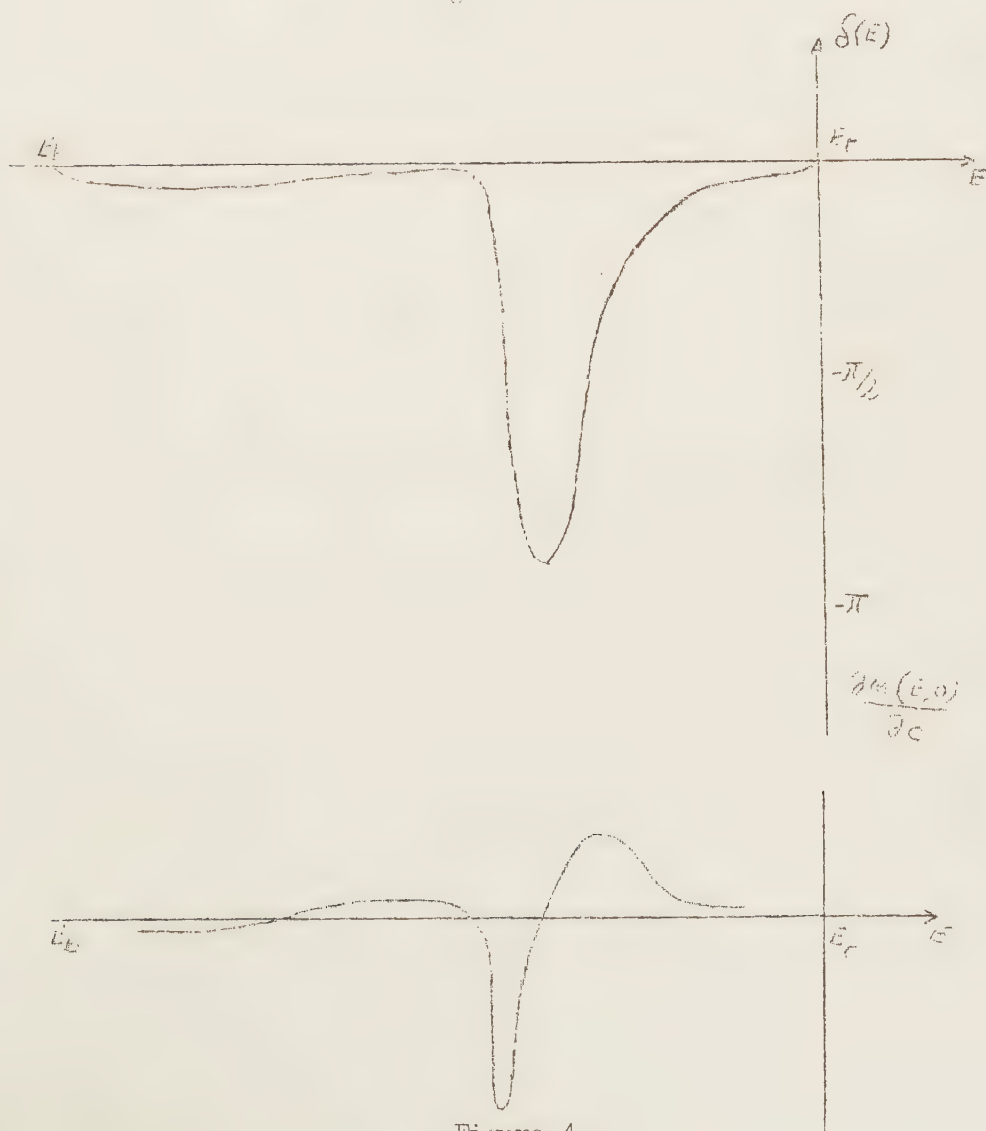
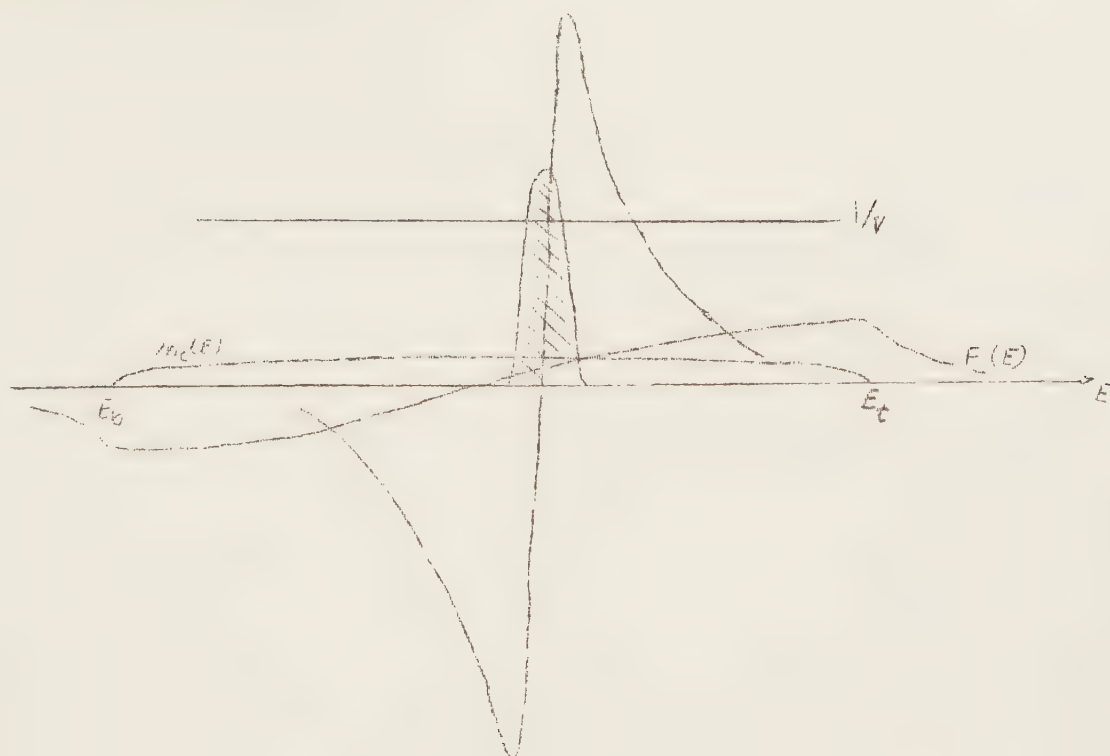


Figure 3



Figuro 4

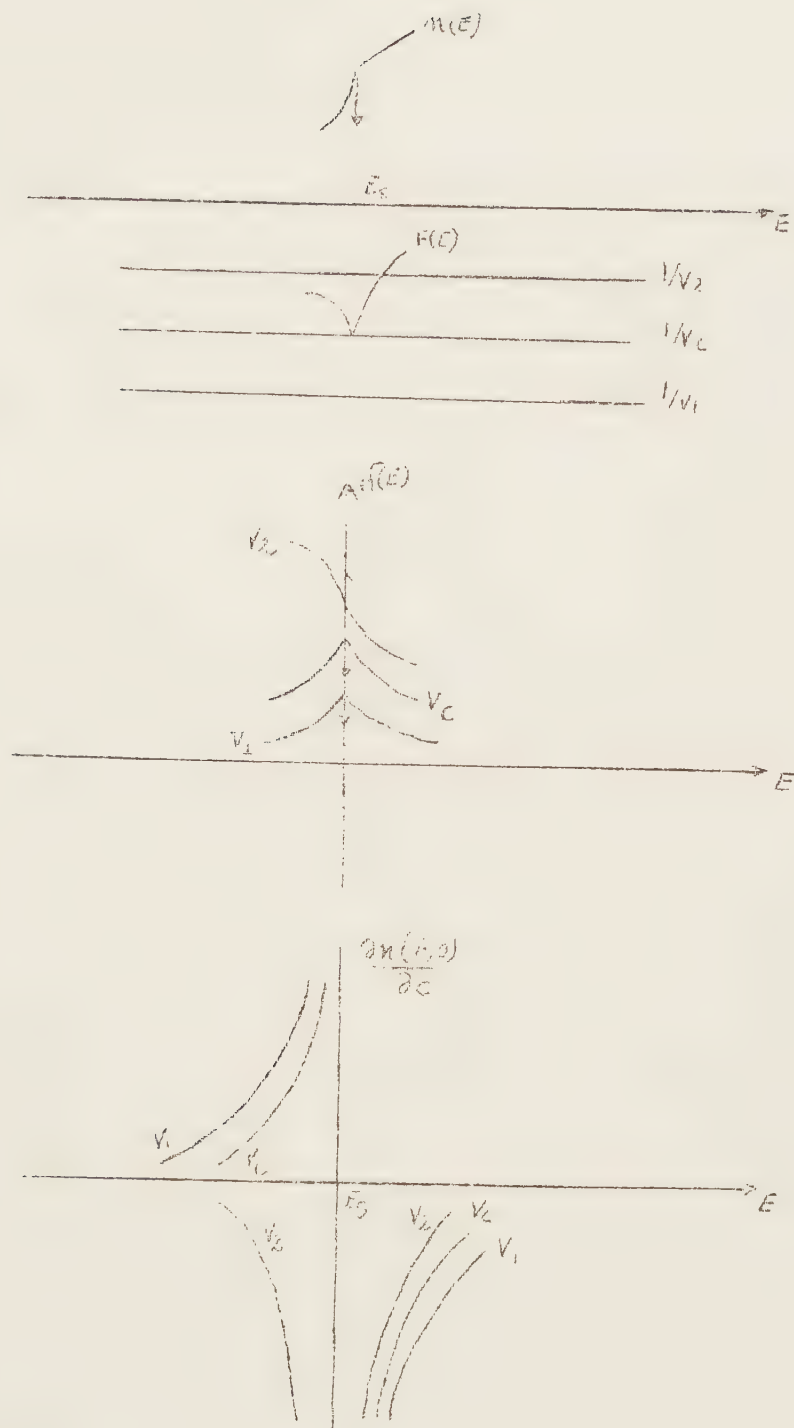


Figure 5.a

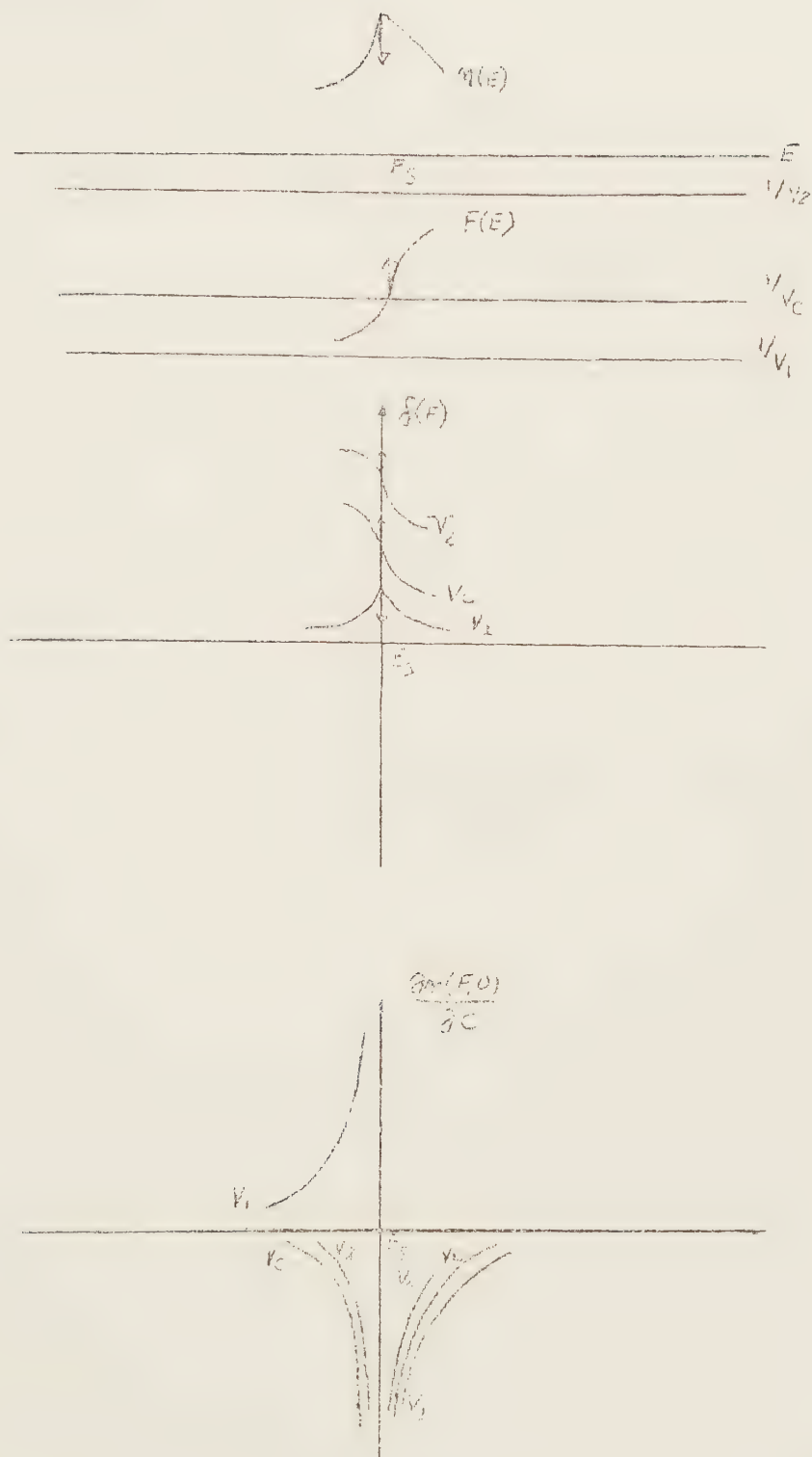


Figure 5.b

CHAPITRE II

MOMENT MAGNETIQUE DES IMPURETES DISSOUTES DANS LES METAUX
FERROMAGNETIQUES

Submitted to "Proc. Phys. Soc."

MAGNETIC MOMENTS OF IMPURITIES IN FERROMAGNETIC TRANSITIONAL ALLOYS

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Abstract

The magnetic moment of the impurity atoms in dilute ferromagnetic transition alloys is calculated from the scattering of d-electrons by spin dependent Hartree-Fock potentials.

The spin dependent potentials are determined self-consistently by imposing Friedel's screening condition and the Hartree Fock relation between up and down spin potentials.

It turns out from this calculation that the impurity negative magnetic moments are due to the repulsion of a bound state above the Fermi level.

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INTRODUCTION.

Ferromagnetic alloys have been intensively studied in recent years, in particular from the point of view of neutron scattering, Low and Collins 1964, 1965, Campbell 1966.

A careful analysis of the neutron diffraction data allows a good knowledge of the impurity magnetic moments, both in magnitude and sign, (Campbell 1966).

These results are available of Fe, Co and Ni alloys.

It turns out that certain impurities of the 3d-transition series when dissolved in the above metals have a negative magnetic moment respect to the host metal magnetic moment (Fig. 13). From these results it becomes apparent that the usual discussion of ferromagnetic alloys in terms of a Hartree picture for the scattering potential does not account for the observed results.

Kanamori, 1965 discussed Ni alloys introducing Hartree-Fock potential for the electron scattering and was able by a suitable self-consistent calculation, to explain the general trend of the observed results, and to give a more detailed description of the model of Friedel, 1958, for these alloys. Here we introduce a slightly different method where Kanamori's neutrality condition within the impurity atom is replaced by Friedel's self-consistency condition for the total displaced charge. We suggest that the last method, given the difficulties of such simplified picture, corresponds better to the physical situation.

Using this model, one is able to describe rather well the observed data for Fe, Co and Ni alloys.

In parts I and II we introduce the hypothesis of the model and the main results that will be used latter. Part III is the description of the properties of Ni, Co and Fe alloys as far the impurity moment is concerned.

Finally parts IV and V are respectively the numerical results and the discussion. In the appendix, as a by product of these calculations, we describe some properties of the moment induced by a local magnetic field at the central cell.

I - DESCRIPTION OF THE MODEL.

I.a.) - Adopted band structure.

The unperturbed d-band of these metals is described in the tight binding approximation, the s-d mixing that is present in the metals being completely neglected.

A qualitative discussion of the effect of s-d mixing in certain cases will be given later. Even in the simple case of a pure d-band an additional difficulty appears due to the presence in the d-band of a five-fold degeneracy.

General methods have been proposed to discuss the scattering of degenerate d-electrons by impurity atoms (Kanamori 1965, Gautier and Lenglet 1965, Callaway 1964).

Unfortunately these methods suppose the knowledge of a detailed energy distribution of the orbitals of given symmetry, even in the simplest case of Hartree potentials ; the situation becomes much more complicated if one intends to introduce Hartree-Fock potentials, because a detailed knowledge of the exchange integrals between several d-orbitals is also required.

Then, for the sake of simplicity we take a d-band made of five equal and independent sub-bands. In this case the scattering is simply treated and the Hartree-Fock effects may be included using only an averaged exchange integral.

We expect that these approximations will not destroy the essential features of the physical situation.

The ferromagnetism of the pure metals will be described in a simple Stoner model by two spin subbands split by the averaged exchange energy.

Within the adopted approximation (cf. below) of a localized impurity potential, the band structure appears only through the density of states.

Then, several models for the density of states were used in the numerical calculation in order to see the dependence of the results in the adopted band shape.

These models are shown schematically in Fig. 1.a, 1.b. and 1.c.

The band widths were taken equal to 4 eV and these density of states are normalized to five electrons p/ atom. Fig. 1.a, 1.b and 1.c represent respectively two pieces of $E^{1/2}$, $E^{3/2}$ and $(1 - \frac{E^2}{\Delta^2})$ curves.

I.b.) - Description of the impurity potential.

We use a phenomenological approach in the following sense : let's assume a localized, spin dependent potential $V_{\sigma}(\vec{r})$ (σ designates the spin).

Using the hypothesis of the localization of $V_{\sigma}(\vec{r})$, one calculates easily the scattering of the d-electrons and consequently the change in occupation number of the σ orbitals. Then, within the Hartree-Fock scheme, the σ matrix element of $V_{\sigma}(\vec{r})$ is given by the bare Coulomb potential due to the charge difference plus the change due to the impurity in the Coulomb and exchange interactions.

Since the Coulomb interaction is the same for both spin directions, the difference $V_{\uparrow} - V_{\downarrow}$ depends only on the exchange integral J and on the difference between the changes in occupation number of the $\uparrow$ and $\downarrow$ impurity orbitals, that means

$$V_{\uparrow} - V_{\downarrow} = - J(\Delta N_{\uparrow} - \Delta N_{\downarrow}) \quad (1)$$

with $\Delta N_{\sigma} = N_{\sigma}(V_{\sigma}) - N_{\sigma}(0)$

$N_{\sigma}(V_{\sigma})$ is the total impurity occupation number, determined by the potential V_{σ} . As it will be seen in next part $N_{\sigma}(V_{\sigma})$ contains the contributions of the scattered states of the continuum plus the amplitude at the impurity of the bound state eventually present.

$N_{\sigma}(0)$ is just the occupation number of the unperturbed orbitals.

This formulation presents the advantage that the Coulomb interaction U , very difficult to estimate due to correlations, cancels out.

We want to stress that expression (1) depends on the assumption that the value of the exchange integral in the host metal is taken equal to that at the impurity site.

We expect that this is not a bad approximation for impurities in

the same transition series.

In this case the exchange coefficient can be estimated from the splitting of the spin subbands in the host metal. Equation (1) gives a relation between the matrix elements of $V_{\uparrow}$ and $V_{\downarrow}$. The phenomenological approach is completed by Friedel's screening condition

$$Z = Z_{\uparrow}(V_{\uparrow}) + Z_{\downarrow}(V_{\downarrow}) \quad (2)$$

where $Z_{\sigma}(V_{\sigma})$ is the charge displaced by the potential V_{σ} is the σ sub-band. Within the limitations of this picture, $V_{\uparrow}$ and $V_{\downarrow}$ can be determined self-consistently from relations (1) and (2).

II - PRINCIPAL RESULTS AND PROPERTIES.

II.a.) Friedel's screening condition.

We divide this discussion in two topics : 1) two partially filled sub-bands, 2) one completely filled sub-band.

1) Case of two partially filled sub-bands.

Within the assumptions of paragraph I.a), i.e., five independent sub-bands, the total displaced charge must be :

$$Z = -\frac{5}{\pi} \sum_{\sigma} \arctg \frac{\pi n_{\sigma}(\epsilon_F) V_{\sigma}/5}{1 - V_{\sigma} F_{\sigma}(\epsilon_F)/5} \quad (3)$$

where $n_{\sigma}(\epsilon)$ is the total density of states in the d-band, $F_{\sigma}(\epsilon)$ its Hilbert transform and Z the excess charge introduced by the impurity. Expression (3) gives the relation between $V_{\uparrow}$ and $V_{\downarrow}$ that is imposed by the charge neutrality condition.

It turns out that the form of the relation $V_{\uparrow} = f(V_{\downarrow}, Z)$ as derived from (3) is that of one branch of hyperbola. In fact, a little algebra shows that (3) can be written as

$$\alpha_1 + \alpha_2 V_{\downarrow} + \alpha_3 V_{\uparrow} + \alpha_4 V_{\uparrow} V_{\downarrow} = 0 \quad (4)$$

where the α_i are combinations of $n_\sigma(\epsilon_F)$, $F_\sigma(\epsilon_F)$ and $\text{tg} \frac{\pi Z}{5}$

Then a coordinate transformation $V_\sigma \rightarrow \bar{V}_\sigma$ put (4) in the form

$$\bar{V}_\uparrow \bar{V}_\downarrow = \text{constant} \quad (5)$$

which is the announced hyperbolic dependence.

In Fig.2 we show as an example the relation $V_\uparrow = f(V_\downarrow, Z)$, for several values of Z in the case of Fe.

This curve is calculated numerically using the density of states of Fig. 1.c.

2) Case of one completely filled sub-band.

The up-spin band is supposed to be filled and the Fermi level to lie above the top of the band (cf. fig.3). The essential difference with respect to the previous case is that $Z_\uparrow$ may have only two values.

In fact, for values of $V_\uparrow$ not strong enough to push a $\uparrow$ spin bound state across the Fermi level, the total $\uparrow$ spin displaced charge is zero.

Let's call $V_\uparrow^{\text{crit}}$ the potential such that $1/V_\uparrow^{\text{crit}} = F_\uparrow(\epsilon_F)/5$. Then for $V_\uparrow < V_\uparrow^{\text{crit}}$ it follows that $Z_\uparrow = 0$.

However for $V_\uparrow > V_\uparrow^{\text{crit}}$, the bound state has crossed the Fermi level, and the displaced charge is now -5. Let $-Z_m$ ($Z_m > 0$) to the maximum charge that can be repelled by the $\uparrow$ spin band. This is obtained for an infinitely repulsive potential $V_\downarrow = +\infty$:

$$-Z_m = -\frac{5}{\pi} \text{arctg} \frac{\pi n_\downarrow(\epsilon_F)}{F_\downarrow(\epsilon_F)} \quad (6)$$

Using these results one can construct easily the curve $V_\uparrow = f(V_\downarrow, Z)$ (Fig.4). Suppose first $|Z| < Z_m$ ($Z < 0$). For $V_\uparrow < V_\uparrow^{\text{crit}}$, screening is completely performed in the $\downarrow$ spin band and consequently the relation $V_\uparrow = f(V_\downarrow, Z)$ is a series of lines parallel to the $V_\uparrow$ axis (Fig.4). When Z tends to $-Z_m$, the corresponding line tends to infinity. The situation $V_\uparrow > V_\uparrow^{\text{crit}}$ however, is not compatible with $|Z| < Z_m$. In fact, the total displaced charge is given in this case by

$Z = -5 + Z_{\downarrow}(V_{\downarrow})$ and for $V_{\downarrow}$ varying between $-\infty$ and $+\infty$, $Z_{\downarrow}$ varies between $5 - Z_m$ and $-Z_m$ (cf (3)). Then the only charges that can be screened vary between $-Z_m$ and $5 - Z_m$, and the condition $|Z| < Z_m$ can never be satisfied.

In conclusion, for $|Z| < Z_m$, the possible solutions lie in the region defined by $V_{\uparrow} < V_{\uparrow}^{\text{crit}}$ and $0 < V_{\downarrow} < +\infty$ (cf. Fig. 4).

Suppose now $|Z| > Z_m$. Here the situation is inversed since it is impossible to screen the charge without pushing the bound state across the Fermi level. Then the region of solutions is defined by $V_{\uparrow} > V_{\uparrow}^{\text{crit}}$. It is to be noted that the maximum charge that can be screened within this picture is $-5 - Z_m$. In Fig. 4, a schematic behaviour of these curves is given for $Z_m = +3.5$.

II.b.) Occupation number of the impurity orbitals.

We divide this paragraph into three parts. In part 1) we present the contributions to the impurity orbital occupation and a theorem relating them. In parts 2) and 3) we discuss respectively the properties of the impurity orbital occupation as a function of V_{σ} and the particular case of metals with one completely filled sub-band.

1) General results.

The occupation number of the impurity orbitals is in general made up of two contributions

- i) From the continuous spectrum via the amplitude at the impurity of the occupied scattering states.
- ii) Amplitude at the impurity site of the bound states eventually present. The contribution i) turns out to be given by :

$$N_{\sigma}^{\text{scatt}}(V_{\sigma}) = \int_0^{\epsilon_F} \frac{n_{\sigma}(\epsilon) d\epsilon}{[1 - V_{\sigma} F_{\sigma}(\epsilon)/5]^2 + [\pi V_{\sigma} n_{\sigma}(\epsilon)/5]^2} \quad (7)$$

and only involves the occupied part of the band. The other contribution ii)

is given by

$$N_{\sigma}^{\text{bound}}(V_{\sigma}) = \frac{F_{\sigma}^2(E_{\sigma\sigma})}{\left| \frac{dF}{d\varepsilon}(E_{\sigma\sigma}) \right|} \quad (8) \quad \text{where } E_{\sigma\sigma} \text{ is defined by } 1 - V_{\sigma} F_{\sigma}(E_{\sigma\sigma})/5 = 0$$

If the bound states are eventually present and occupied the total occupation number is given by the sum of (7) and (8). Before discussing the properties of (7) and (8) let's recall a theorem (6) that will be useful in a next discussion :

$$\int_{\text{band}} d\varepsilon \{ |\psi_{\text{scatt}}(\varepsilon, \vec{r})|^2 - |\psi_0(\varepsilon, \vec{r})|^2 \} + \sum_{E_i} |\psi_{\text{bound}}(E_i, \vec{r})|^2 = 0 \quad (9)$$

where ψ_{scatt} , ψ_{bound} and ψ_0 are respectively tight binding wave functions of the scattered states, bound states and unperturbed states.

This theorem is generally valid within the tight-binding spirit, since it depends only on the fact that the perturbed and unperturbed states form complete sets.

2) Properties of the functions (7) and (8).

The asymptotic behaviour of (6) is :

i) For $V_{\sigma} = 0$ one obtains the unperturbed occupation number

$$N_{\sigma}^{\text{scatt}}(0) = \int_0^{\varepsilon_F} n(\varepsilon) d\varepsilon$$

ii) For $V_{\sigma} \rightarrow +\infty$, $N_{\sigma}^{\text{scatt}}(V_{\sigma}) \rightarrow 0$; this corresponds to the emptying of the impurity orbital.

iii) For $V_{\sigma} \rightarrow -\infty$, also $N_{\sigma}^{\text{scatt}}(V_{\sigma}) \rightarrow 0$

In the last case iii) a bound state appears below the bottom of the d -band for a potential $V_{\sigma}^{\text{crit}} = \frac{1}{F_{\sigma}(E_{\text{bot}})}$ and this state is certainly

occupied.

Then the occupation number for $|V_\sigma| > |V_\sigma^{\text{crit}}|$ is given the sum of (7) and (8). Since the scattered states contribution tends to zero, the total occupation number in the limit $V_\sigma \rightarrow -\infty$ is determined only by the asymptotic behaviour of (8). From the fact that for large $E_{\text{bot}} - E_\sigma$ the function $F_\sigma(E_{\text{bot}}) \approx \frac{1}{E_{\text{bot}} - E_\sigma} \int n(\epsilon) d\epsilon$ one sees that $N_\sigma^{\text{bound}}(V_\sigma) \rightarrow 5$, which corresponds to a c_{cs} five fold degenerate local state at the impurity site.

iiii) The contribution from the scattered states can be related to the phase shifts $\delta_\sigma(E, V_\sigma)$ in the following way :

$$N_\sigma^{\text{scatt}}(V_\sigma) = -\frac{1}{\pi} \frac{d}{dV_\sigma} \int_0^{\epsilon_F} \delta_\sigma(\epsilon, V_\sigma) d\epsilon \quad (10)$$

This means that N_σ^{scatt} is proportional to the rate of change of the area defined by the ϵ axis, the $\delta_\sigma(\epsilon, V_\sigma)$ curve and the Fermi level. The interest of (10) is that it provides a qualitative discussion of the behaviour of N_σ^{scatt} as a function of V_σ and ϵ_F when a repulsive potential is applied. The schematic behaviour of the phase shift for usual band shapes is given in Fig.5. Let's consider for example the two indicated positions of the Fermi level. In the case of ϵ_{F1} , when V_σ starts increasing from zero, one observes a small change in the occupation number, because the area is not changing rapidly with V_σ (cf. Fig.5 and 6). On the contrary, for values of V_σ around $V_\sigma^{\text{crit}} = \frac{1}{F_\sigma(E_{\text{tcp}})}$, the critical value for repelling a bound state, the phase shift changes from 0 to $-\pi$, producing a big change in the area (cf Fig.5).

Then, the crossing of this potential range is accompanied by a large and sharp decrease of $N_\sigma^{\text{scatt}}(V_\sigma)$, after what the change becomes again rather smooth (Fig.6).

The situation is rather different for E_{F2} , since in this energy region there is only a smooth variation of the phase shift with V_σ (cf Fig.5). Consequently $N_\sigma^{\text{scatt}}(V_\sigma)$ varies smoothly with V_σ as indicated in Fig.6. These qualitative predictions are confirmed by numerical analysis.

3) Completely filled spin sub-band.

Here we discuss the case where the Fermi level lies above the top of one spin sub-band (Fig.3), as in Ni and Co cases.

This is a direct application of theorem⁽⁹⁾.

Suppose V_σ varying between $-\infty$ and $+\infty$. For negative values of V_σ , all the possible values of $E_{0\sigma}$ (energy of the subtracted bound state) lie below the Fermi level and consequently the occupation of the impurity orbital is constant and equal to the unperturbed value (cf Fig.7).

If V_σ becomes positive one has two possibilities:

i) $0 < V_\sigma < \frac{1}{F_\sigma(\epsilon_F)}$. In this case the created bound state lies below the Fermi level and the occupation number is still constant and equal to the value for $V_\sigma < 0$

ii) $V_\sigma > \frac{1}{F_\sigma(\epsilon_F)}$. The situation changes because the bound state lies above the Fermi level and theorem⁽⁹⁾ gives a change in occupation number equal to

$$- F^2(E_{0\sigma}) / |dF(E_{0\sigma})/dE| \quad (\text{cf Fig.7})$$

There is consequently a discontinuity in the occupation number and its derivative $\frac{dN_\sigma}{dV_\sigma}$ as shown schematically in Fig.7.

III - EXCHANGE SELF-CONSISTENCY CONDITION.

In this paragraph we want to discuss some general properties of equation (1) and then consider the particular cases of one filled spin sub-band, and two partially filled sub-bands.

In this way, part II.a) contains the general results, part II.b) is a discussion of Ni and Co cases and finally part II.c) considers Fe case.

III.a.) General properties of equation (1).

Equation (1) can be written in the following way :

$$f_{\uparrow}(V_{\uparrow}) = f_{\downarrow}(V_{\downarrow}) \quad (11) \quad \text{where } f_{\sigma}(V_{\sigma}) = V_{\sigma} + J(N_{\sigma}(V_{\sigma}) - N_{\sigma}(0))$$

From (10) the following results can be obtained :

1) Asymptots of the relation $V_{\uparrow} = f(V_{\downarrow}, J)$

Since for $V_{\sigma} \rightarrow +\infty$, $N_{\sigma}(V_{\sigma}) \rightarrow 0$ and for $V_{\sigma} \rightarrow -\infty$, $N_{\sigma}(V_{\sigma}) \rightarrow N_{\sigma}(0)$ one obtains two asymptots :

$$V_{\uparrow} = V_{\downarrow} + Jn_h \quad \text{for } \{V_{\uparrow}, V_{\downarrow}\} \rightarrow +\infty$$

$$V_{\uparrow} = V_{\downarrow} \quad \text{for } \{V_{\uparrow}, V_{\downarrow}\} \rightarrow -\infty$$

where $n_h = N_{\uparrow}(0) - N_{\downarrow}(0)$ is the magnetic moment per atom in the matrix (in Bohr magnetons).

2) A very simple necessary condition for the occurrence of a negative local moments follows from equation (9) :

In fact,

$$-J(N_{\uparrow}(V_{\uparrow}) - N_{\downarrow}(V_{\downarrow})) = V_{\uparrow} - V_{\downarrow} - Jn_h$$

Then if $N_{\uparrow}(V_{\uparrow}) < N_{\downarrow}(V_{\downarrow})$ one has :

$$V_{\uparrow} > V_{\downarrow} + Jn_h \quad (12)$$

The asymptot $V_{\uparrow} = V_{\downarrow} + Jn_h$ divides then the plane $V_{\uparrow}, V_{\downarrow}$ into two regions, only one of them being able to produce negative local moments.

It should be stressed that this is only a necessary condition ; one should include the screening condition to determine in which portions of this half plane the self-consistent solution exists.

3) The derivative $\frac{dV_{\uparrow}}{dV_{\downarrow}}$ can be deduced from (10) to give :

$$\frac{dV_{\uparrow}}{dV_{\downarrow}} = \frac{1 + J \frac{dN_{\downarrow}}{dV_{\downarrow}}}{1 + J \frac{dN_{\uparrow}}{dV_{\uparrow}}} \quad (13)$$

From (3.3) one can derive the relative extremal points of the $V_{\uparrow} = f(V_{\downarrow}, J)$ function and also the points where $\frac{dV_{\uparrow}}{dV_{\downarrow}}$ is infinite.

The latter points, given by $1 + J \frac{dN_{\uparrow}}{dV_{\uparrow}}$, are very important since $\frac{dV_{\downarrow}}{dV_{\uparrow}}$, changes sign there, provided that the following conditions are satisfied:

i) The $\uparrow$ spin sub-band is almost filled

ii) The $\downarrow$ spin sub-band is half filled

iii) The exchange integral is not large.

From the condition i) and the discussions of II.b.2) it follows that $N_{\uparrow}(V_{\uparrow})$ varies smoothly with $V_{\uparrow}$ except in a narrow potential range (cf Fig.6).

In this situation $\frac{dN_{\uparrow}}{dV_{\uparrow}}(V_{\uparrow})$ has a high and narrow peak (cf Fig. 8).

Then the maximum number of solutions of $1 + J \frac{dN_{\uparrow}}{dV_{\uparrow}} = 0$ is two. Lets call these solutions $V_{\uparrow}^{(1)}$ and $V_{\uparrow}^{(2)}$. Evidently $1 + J \frac{dN_{\uparrow}}{dV_{\uparrow}}$ is negative for $V_{\uparrow}^{(1)} < V_{\uparrow} < V_{\uparrow}^{(2)}$ and positive elsewhere (cf Fig.8). On the other hand it follows from condition ii) and the discussions of II.b.2) that $N_{\downarrow}(V_{\downarrow})$ varies smoothly with $V_{\downarrow}$ (cf Fig.6). Consequently, $\frac{dN_{\downarrow}}{dV_{\downarrow}}$ is small for all values of $V_{\downarrow}$ and if condition iii) is valid $1 + J \frac{dN_{\downarrow}}{dV_{\downarrow}}$ has only non negative values.

In conclusion, the sign of $\frac{dV_{\downarrow}}{dV_{\uparrow}}$ is given by the sign of $1 + J \frac{dN_{\uparrow}}{dV_{\uparrow}}$. Now using these results, we can describe qualitatively the effect of the zeros of $\frac{dV_{\downarrow}}{dV_{\uparrow}}$ in the behaviour of $V_{\downarrow} = f(V_{\uparrow}, Z)$.

Suppose $V_{\uparrow} > 0$ and smaller than $V_{\uparrow}^{(1)}$. In this case $\frac{dV_{\downarrow}}{dV_{\uparrow}}$ is positive, and $V_{\downarrow}$ increases monotonically with $V_{\uparrow}$.

Now, for $V_{\uparrow}$ increasing in the interval $V_{\uparrow}^{(1)} < V_{\uparrow} < V_{\uparrow}^{(2)}$, $\frac{dV_{\downarrow}}{dV_{\uparrow}}$ is negative and $V_{\downarrow}$ decreases monotonically reaching even negative values.

Finally for $V_{\uparrow} > V_{\uparrow}^{(2)}$ again $V_{\downarrow}$ increases with increasing $V_{\uparrow}$.

It should be remarked that in the case of one completely filled sub-band there is just one solution of $1 + J \frac{dN_{\uparrow}}{dV_{\uparrow}} = 0$ (cf Fig.7). This anomaly is associated to the existence of a discontinuity in the $N_{\uparrow}(V_{\uparrow})$ function.

III.b.) Discussion of Ni and Co cases.

Now we apply the previous results to give a qualitative description of the solutions of equation(11) when one sub-band is full. This should apply to Ni and Co matrices. First we discuss the form of the f_{σ} functions defined in equation (11). From the results of paragraph II.b.3.) one sees that

$$\text{i) } f_{\uparrow}(V_{\uparrow}) = V_{\uparrow} \quad \text{for } -\infty < V_{\uparrow} < 1/F_{\uparrow}(\epsilon_F) \quad ((14))$$

$$\text{ii) } f_{\uparrow}(V_{\uparrow}) = V_{\uparrow} - J F_{\uparrow}^2(\epsilon_{\uparrow}) / |dF_{\uparrow}(\epsilon_{\uparrow})/dE| \quad \text{for } V_{\uparrow} > \frac{1}{F_{\uparrow}(E_F)}$$

where $E_{\uparrow}$ is the energy of the $\uparrow$ spin bound state.

Equations ((14)) show that the asymptot of $f_{\uparrow}$ for $V_{\uparrow} \rightarrow +\infty$ is $V_{\uparrow} - J N_{\uparrow}(0)$. On the other hand, $f_{\downarrow}(V_{\downarrow}) = V_{\downarrow} + J(N_{\downarrow}(V_{\downarrow}) - N_{\downarrow}(0))$ is a continuous function which has two asymptots :

$$\begin{aligned} V_{\uparrow} - J N_{\downarrow}(0) & \text{ for } V_{\downarrow} \rightarrow +\infty \\ V_{\downarrow} & \text{ for } V_{\downarrow} \rightarrow -\infty \end{aligned} \quad ((15))$$

All these functions are indicated schematically in fig.(9) and their numerical determination will be indicated in the next part.

The method of solution of equation ((11)) consists then in taking a parallel to the V axis, the crossing points with $f_{\uparrow}$ and $f_{\downarrow}$ giving the corresponding values of $V_{\uparrow}$ and $V_{\downarrow}$. The origin of the jump in $V_{\downarrow} = f(V_{\uparrow}, J)$ and its connection to the discontinuity in the occupation number of the $\uparrow$ spin orbital appears clearly in Fig.9. Suppose one increases $V_{\uparrow}$ starting from zero : this corresponds to following the positive part of the straight line ((14)). There is only one, positive valued $V_{\downarrow}$ which increases with increasing $V_{\uparrow}$ (cf Fig.9).

At $V_{\uparrow} = V_{\uparrow}^{\text{crit}} = 1/F_{\uparrow}(\epsilon_F)$, the function $f_{\uparrow}(V_{\uparrow})$ has a discontinuity (12) and there appears suddenly a solution with $V_{\downarrow}$ negative and in the region $V_{\uparrow} > V_{\downarrow} + Jn_h$ when negative local moments may occur.

For $V_{\uparrow} > V_{\uparrow}^{\text{crit}}$ all the solutions $V_{\downarrow}$ lie in the favorable region for negative moments. Fig. 10 gives the schematic behaviour of $V_{\downarrow} = f(V_{\uparrow}, J)$ for Ni and Co cases. This behaviour can be understood in very simple physical grounds. When the bound state crosses the Fermi level, the sudden change produced in the occupation number of the impurity $\uparrow$ spin orbitals determines a local change in the exchange interaction among $\uparrow$ spin electrons.

In order to compensate it, the $\downarrow$ spin potential rearranges itself to increase the occupation number of $\downarrow$ spin impurity orbitals, thus restoring the averaged local exchange interaction.

When $V_{\uparrow}$ increases, the exchange interaction among $\uparrow$ spins electrons at the impurity decreases with the decreasing occupation number. In this situation the potential $V_{\downarrow}$ cannot decrease indefinitely because the averaged local exchange interaction would increase gradually. This explains why for $V_{\uparrow} > V_{\uparrow}^{\text{crit}}$, $V_{\downarrow}$ passes gradually from negative to positive values.

These results (Fig.10) combined with the screening condition (Fig.4) show that the local magnetic moment changes of sign for an increasing excess charge.

In fact, for $|Z| < Z_m$ the crossing points of $V_{\uparrow} = f(V_{\uparrow}, Z)$ and $V_{\uparrow} = f(V_{\downarrow}, J)$ lie in the region defined by $0 < V_{\downarrow} < +\infty$ and $V_{\uparrow} < V_{\uparrow}^{\text{crit}}$ (cf Fig. 10 and 4). But in that region one has only positive magnetic moments because the condition $V_{\uparrow} > V_{\downarrow} + Jn_h$ is not satisfied. On the other hand for $|Z| > Z_m$ the crossing points lie in the region $V_{\uparrow} < V_{\uparrow}^{\text{crit}}$ thus satisfying the condition $V_{\uparrow} > V_{\downarrow} + Jn_h$ for the occurrence of negative moments. This discussion confirms Friedel's description of Ni alloys⁽⁴⁾, which was based on a spin independent perturbing potential ($V_{\uparrow} = V_{\downarrow}$).

III.c.) Discussion of Fe case.

The usually adopted band model of iron consists⁻¹⁵ of an almost filled $\uparrow$ spin sub-band and a half filled $\downarrow$ spin sub-band (Fig.11).

In this case, the presence of holes in both sub-bands avoids discontinuities in the $N_{\sigma}(V_{\sigma})$ and $f_{\sigma}(V_{\sigma})$ curves.

Following the considerations of paragraph II.b.2) one expects the occupation number $N_{\uparrow}(V_{\uparrow})$ to decrease sharply and very rapidly for increasing perturbation around the value of $V_{\uparrow}$ for which a bound state is repelled.

Consequently the region where $\frac{dN_{\uparrow}}{dV_{\uparrow}}$ is large is rather narrow and the points $V_{\downarrow}^{(1)}$ and $V_{\downarrow}^{(2)}$ are close together.

On the other hand, the change in $N_{\downarrow}(V_{\downarrow})$ is expected to be rather smooth since the Fermi level lies around the middle of the $\downarrow$ spin band.

In these conditions Fig. 6 and 8 are appropriate schematic descriptions of the behaviour of these quantities for Fe.

Consequently the assumptions of paragraph III.a.3) are satisfied and one expects an "oscillating" behaviour of $V_{\downarrow}$ for values of $V_{\uparrow}$ around the critical potential for repelling a bound state.

One obtains a behaviour very similar to the Ni and Co cases, with the essential difference that the discontinuous jump is now replaced by a continuous and rapid variation (Fig.12).

The same physical arguments concerning the changes in exchange interaction can be repeated here to understand the behaviour of the $V_{\downarrow} = f(V_{\uparrow}, J)$ curve.

Again these results can be combined with the screening condition (Fig.2) to see that a transition to negative local moments occurs for large enough repulsive perturbations.

IV - NUMERICAL CALCULATIONS AND RESULTS.

Numerical calculations were made for three purposes : to verify quantitatively the preceeding qualitative discussions, the dependence on the particular band shape and to determine precisely the values of the magnetic moments of the impurities. The general considerations which do not involve the exchange interaction turn out to be rather insensitive to the adopted band shapes (Fig. 1.b., 1.c.).

The self-consistent solutions of equations (1) and (2) requires the choice of a value for J .

In the Fe case we adopted $J \approx 0.5$ eV which is consistent with a band width of the order of 4 eV and 2.5 $\downarrow$ spin holes.

For Ni and Co cases, the important parameter in the determination of the self-consistent solutions is the distance between the top of the

occupied sub-band and the Fermi level. Because of the lack of detailed calculations for these metals, we adopted the usually estimated value of 0.2 eV.

This corresponds to J values of the order of 1 eV and 0.9 eV for Ni and Co respectively.

The results of the self-consistent calculation are shown in Fig. 13.a., 13.b., 13.c. respectively for Fe, Co, Ni, together with experimental data.

As a by product of this numerical analysis we calculated the averaged magnetic moment per impurity atom :

$$\frac{du}{dc} = Z_{\uparrow}(V_{\uparrow}) - Z_{\downarrow}(V_{\downarrow}) \quad (16)$$

These results are shown in Fig. 14.a., b., c., as calculated using the density of states 1.c..

V - DISCUSSION.

This highly simplified model provides a qualitative description of the observed data. It explains rather well the general variation with the difference of valency of the magnetic moments observed at the impurity sites; it is shown in particular that the antiferromagnetic moments observed for impurities far enough on the left in the periodic table can always be related to the apparition of empty d bound states above the Fermi level. This confirms for Co and Ni and extends for the Fe case the analysis of Friedel⁽⁴⁾ and Kanamori⁽³⁾.

In cases where one spin sub-band is completely filled the oversimplification of neglecting the s-d broadening of the repelled bound state may produce some difficulties. In fact, for particular choices of the parameters involved, there exists values of Z for which equations (1) and (2) can't be solved simultaneously.

The origin of this difficulty is the discontinuous change of the occupation of the bound state when it crosses the Fermi level.

Since the effect of s-d broadening is to eliminate any discontinuity, the solutions would be found in any case, provided that s-d mixing is included.

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R E F E R E N C E S

- BARDASIS A., FALK O.S., FEPRELL R.A., FULLENBAUM M.S., PRANGE R.E., and
MILLS O.L., 1965, Phys. Rev. Letters, 14 298-300.
- CALLAWAY J., 1964, J. Math. Phys. 5, 783-798.
- CAMPBELL I.A., 1966, Proc. Phys. Soc. 89, 71-76.
- COLLINS M.F., and HOW G.C., 1964, J. Phys. Paris 25, 596-603.
1965, Proc. Phys. Soc. 86, 535-548.
- FRIEDEL J., 1958, Nuovo Cimento 7 Supp. 2, 287-311.
- GAUTIER F. and LENGELART P., 1965, Phys. Rev. 139 A, 705-702.
- KANAMORI J., 1965, J. Appl. Phys. 36, 929-935.
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FIGURE CAPTIONS

- Fig. 1 - Adopted band shapes.
- a) Two pieces of parabolae $\propto \sqrt{E}$
 - b) Two " " $\propto E^{3/2}$ curve
 - c) Two overlapping parabolae $\propto (1 + \frac{E^2}{\Delta^2})$
- Fig. 2 - Relation $V_{\uparrow} = f(V_{\downarrow}, Z)$ for Fe case, calculated using the density of states 1 c.
- Fig. 3 - Schematic band structure of Ni and Co.
- Fig. 4 - Relation $V_{\uparrow} = f(V_{\downarrow}, Z)$ for the case of one completely filled spin sub-band ($Z_m = 3.5$) (schematic).
- Fig. 5 - Schematic behaviour of the phase shift $\delta_{\sigma}(E, V_{\sigma})$ as a function of energy, for several values of the potential ($V_1 < V_2 < V_{\text{crit}} < V_3 < V_4$).
- Fig. 6 - $N_{\sigma}^{\text{scatt}}(V_{\sigma}, \epsilon_F)$ as a function of the potential V_{σ} for two positions of the Fermi level : almost filled bands (ϵ_{F1}) and half filled bands (ϵ_{F2}) (schematic).
- Fig. 7 - Total occupation number $N_{\sigma}(V_{\sigma})$ and its derivation $\frac{dN_{\sigma}}{dV_{\sigma}}$ as a function of the potential for the case of one completely filled spin sub-band. (schematic).
- Fig. 8 - $\frac{dN_{\sigma}}{dV_{\sigma}}$ as a function of the potential for almost filled bands (ϵ_{F1}) and half-filled bands (ϵ_{F2}) (schematic).
- Fig. 9 - Schematic behaviour of the functions f for the case of one completely filled sub-band. Two solutions ($[V_{\uparrow}^a, V_{\uparrow}^a]$ and $[V_{\uparrow}^b, V_{\downarrow}^b]$) of equation $f_{\uparrow} = f_{\downarrow}$ are also indicated.
- Fig. 10 - Schematic behaviour of the relation $V_{\uparrow} = f(V_{\downarrow}, J)$ for the case of one completely filled sub-band.
- Fig. 11 - Schematic band structure of Fe.
- Fig. 12 - Schematic behaviour of the relation $V_{\uparrow} = f(V_{\downarrow}, J)$ for Fe case.

Fig. 13 .. Numerical results and observed data
and 14 a) Fe case b) Ni case c) Co case.

Fig. A1 - Band structure corresponding to a broad band $n_1(\epsilon)$ plus a sharp and high peak. The functions $F_1(\epsilon)$ and $F_p(\epsilon)$ are also indicated (schematic).

Fig. A2 - Derivative $\frac{dA(\epsilon)}{dE}$ as a function of energy for the case of a peak

Fig. A3 -- Function $A(\epsilon)$ as a function of energy for the case of a peak.

APPENDIX

Magnetic moment induced by a local magnetic field

We want to discuss the magnetic moment induced at the origin by a local magnetic field $H = H_0 \delta(\vec{r})$ as a function of the band structure.

A - Recall of the formulae.

In the linear approximation, and for the independent particles model

$$\begin{aligned} M(\vec{r}) &= \int \chi(\vec{r} - \vec{r}') H(\vec{r}') d\vec{r}' \\ M(\vec{q}) &= \chi(\vec{q}) H(\vec{q}), \text{ with } \chi(\vec{q}) = \frac{1}{2}(g_e \mu_\beta)^2 G(\vec{q}) \end{aligned} \quad (\text{A.1})$$

where $G(\vec{q})$ is defined by :

$$G(\vec{q}) = \frac{\Omega}{(2\pi)^3} \int_{(E_F)}^{} d\vec{k} \left\{ \frac{1}{E(\vec{k}-\vec{q}) - E(\vec{k}) - i\epsilon} + \frac{1}{E(\vec{k}-\vec{q}) - E(\vec{k}) + i\epsilon} \right\}$$

In terms of $\chi(\vec{q})$ the magnetic moment at the origin, for $H = H_0 \delta(\vec{r})$ is

$$M(0) = H_0 \sum_{\vec{q}} \chi(\vec{q}) \quad (\text{A.2})$$

Expression (A.2) may be written as :

$$\frac{M(0)}{H_0} = -(g_e \mu_\beta)^2 \int_0^{E_F} F(\epsilon) n(\epsilon) d\epsilon \quad (\text{A.3})$$

B - Discussion of the properties of the function $A(\epsilon) = \int_0^\epsilon F(\epsilon') n(\epsilon') d\epsilon'$

B.1) If ϵ_t is the top of the band, $A(E_t) = 0$ provided that $n(\epsilon_t) = 0$

Proof :

$$F(\epsilon) = P \int_0^{\epsilon_t} \frac{n(\epsilon') d\epsilon'}{\epsilon - \epsilon'} = \lim_{\delta \rightarrow 0} \int_0^{\epsilon_t} \frac{(\epsilon - \epsilon') n(\epsilon') d\epsilon'}{(\epsilon - \epsilon')^2 + \delta^2}$$

Now assuming that the two limit processes are interchangeable (regular $n(\epsilon)$) one has :

$$A(\epsilon_t) = \lim_{\delta \rightarrow 0} \int_0^{\epsilon_t} \int_0^{\epsilon_t} \frac{(\epsilon - \epsilon') n(\epsilon') n(\epsilon) d\epsilon d\epsilon'}{(\epsilon - \epsilon')^2 + \delta^2} = - \lim_{\delta \rightarrow 0} \int_0^{\epsilon_t} \int_0^{\epsilon_t} \frac{(\epsilon' - \epsilon) n(\epsilon) n(\epsilon') d\epsilon d\epsilon'}{(\epsilon' - \epsilon)^2 + \delta^2} = -A(\epsilon_t)$$

Then $A(\epsilon_t) = 0$

B.2) The response to a local field is completely defined by the structure of the unoccupied part of the band

Proof : From B1)

$$A(\epsilon_t) = 0 = \int_0^{\epsilon_t} F(\epsilon) n(\epsilon) d\epsilon = \int_0^{\epsilon_F} F(\epsilon) n(\epsilon) d\epsilon + \int_0^{\epsilon_F} F(\epsilon) n(\epsilon) d\epsilon \text{ and then}$$

$$\frac{M(0)}{H_0} = (g_e \mu_B)^2 \int_{\epsilon_F}^{\epsilon_t} F(\epsilon) n(\epsilon) d\epsilon \quad B(1)$$

B.3) The extremal points of $A(\epsilon)$ are given by the zeros of the $F(\epsilon)$ function. In fact

$$\frac{dA}{d\epsilon} = \frac{d}{d\epsilon} \int_0^{\epsilon} F(\epsilon') n(\epsilon') d\epsilon' = F(\epsilon) n(\epsilon) = 0 \quad (B.2)$$

As the state density is in general non vanishing except at the boundaries of the band, $\frac{dA}{d\epsilon} = 0$ implies $F(\epsilon) = 0$.

For bounded $F(\epsilon)$ functions, the number of zeros is always an odd number. This follows because $F(\epsilon)$ is a continuous function, and has opposite sign in the boundaries of the band.

B.4) Effect of a peak in the state density.

Suppose one superposes a high and sharp peak to a smooth density of states curve Fig. A.1.

The $F(\epsilon)$ function is then the superposition of two contributions

$$F(\epsilon) = F_l(\epsilon) + F_p(\epsilon)$$

Around the position of the peak the contribution of $F_p(\epsilon)$ is the dominant and one has for the derivative $\frac{dA}{dE} = F(\epsilon) n(\epsilon)$ the schematic behaviour of Fig. A.2. This rapid variation of the derivative implies in the behaviour represented schematically in fig A.3 for the function $A(E)$.

One can note the dissymmetry of the $A(\epsilon)$ function around the center of the peak.

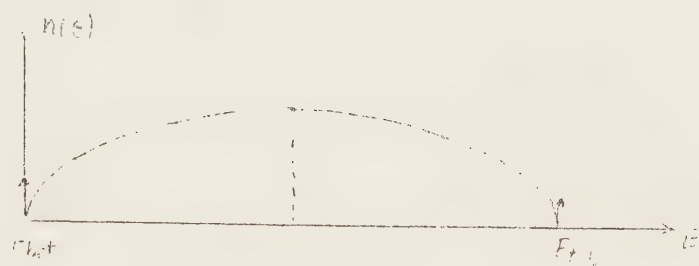


fig 1a

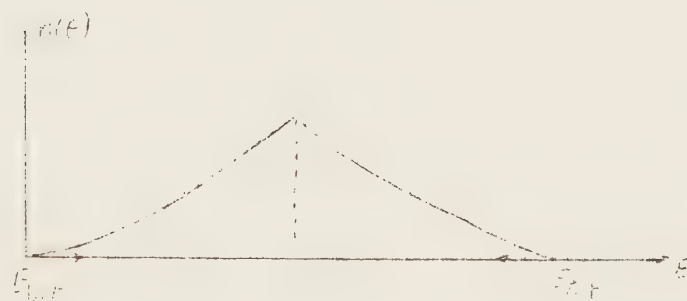
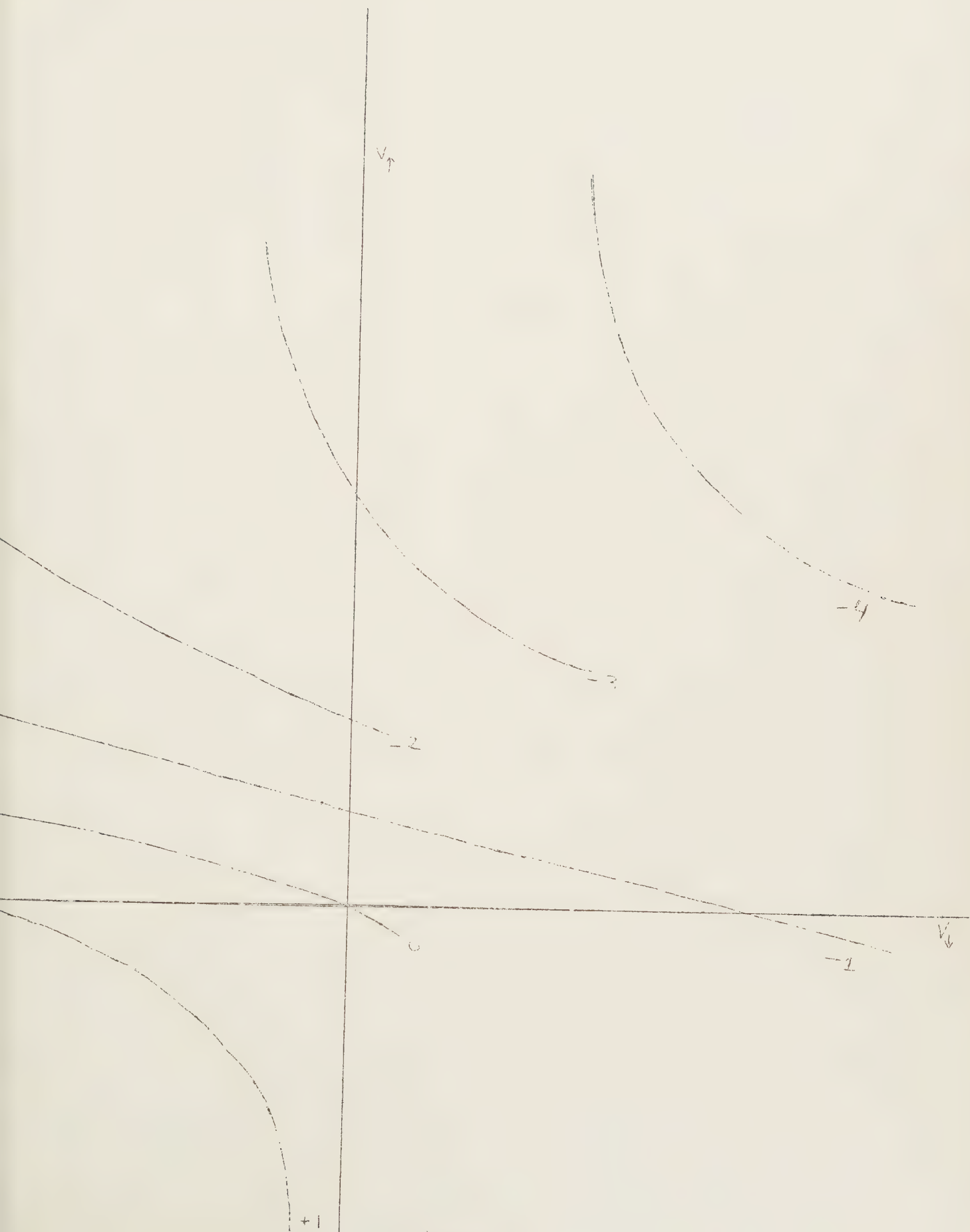


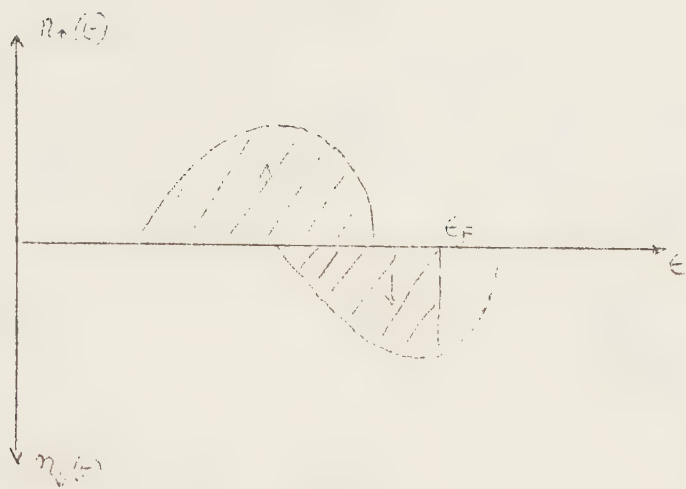
fig 1b



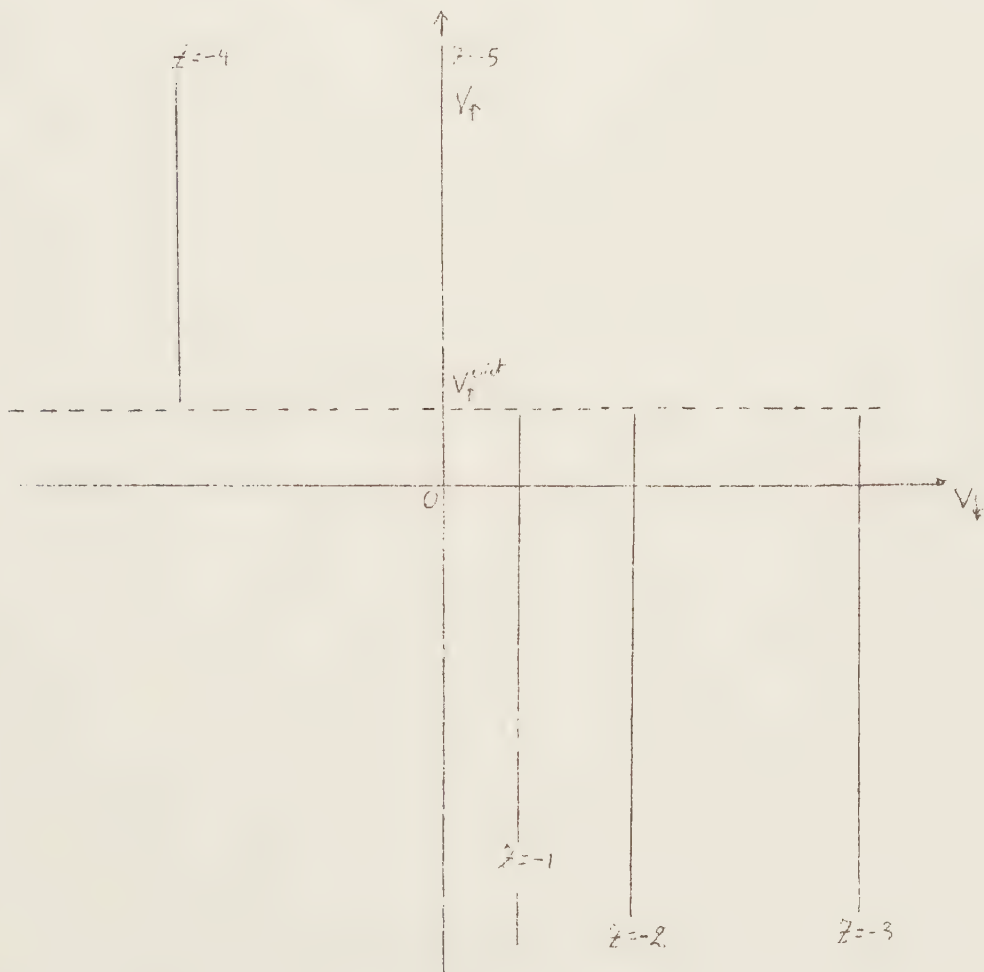
fig 1c



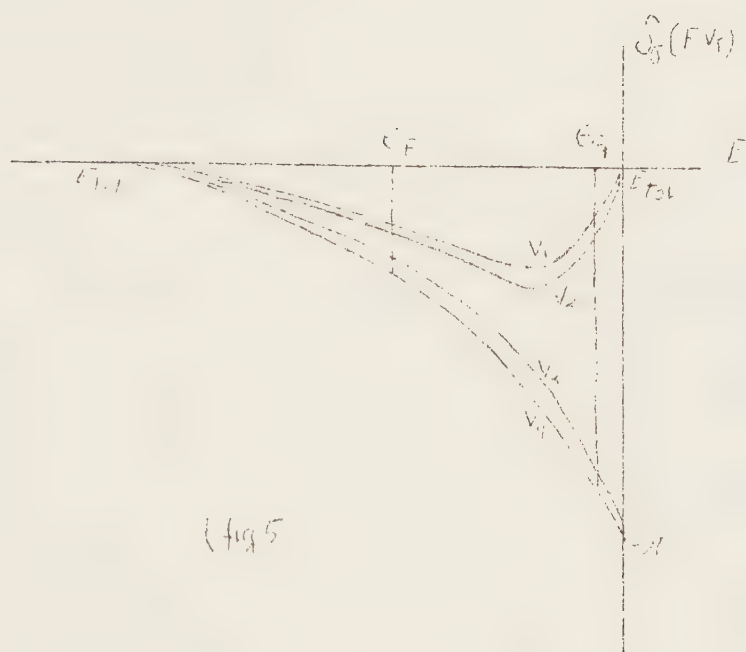
(fig 2)



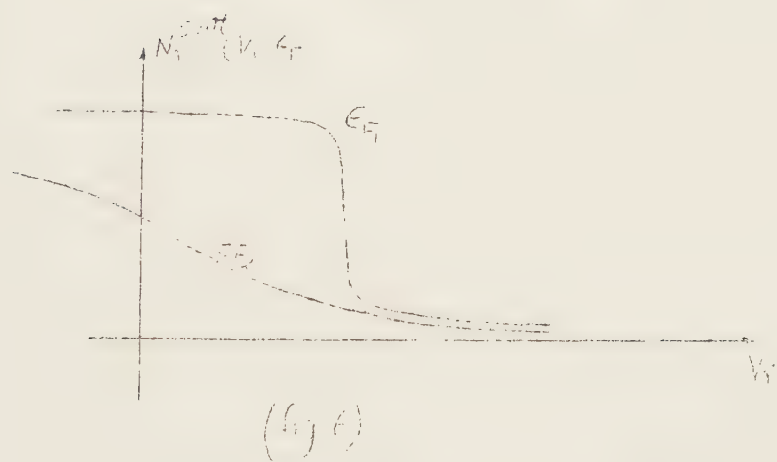
(fig 3)



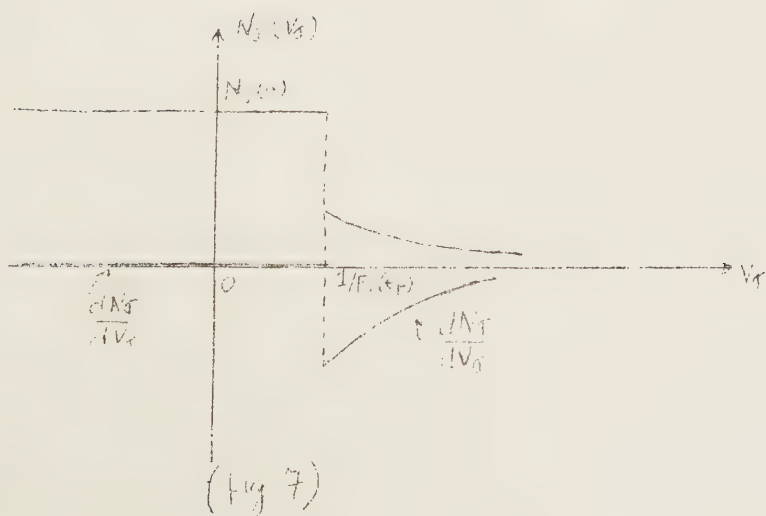
(fig 4)



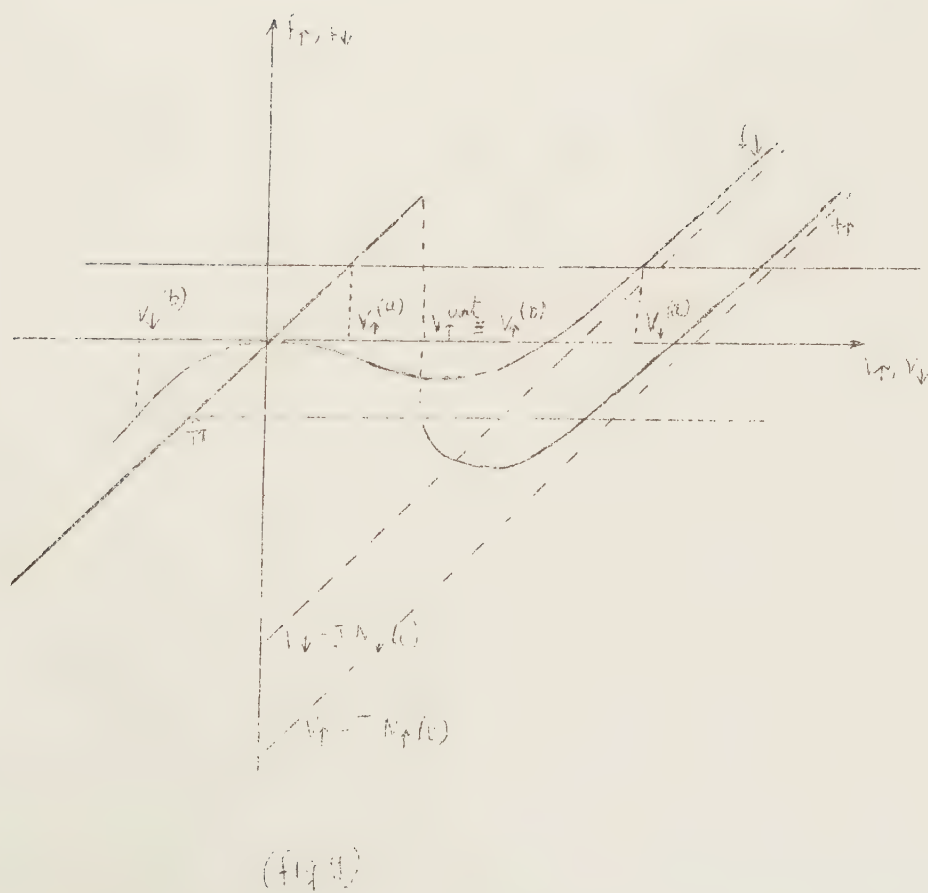
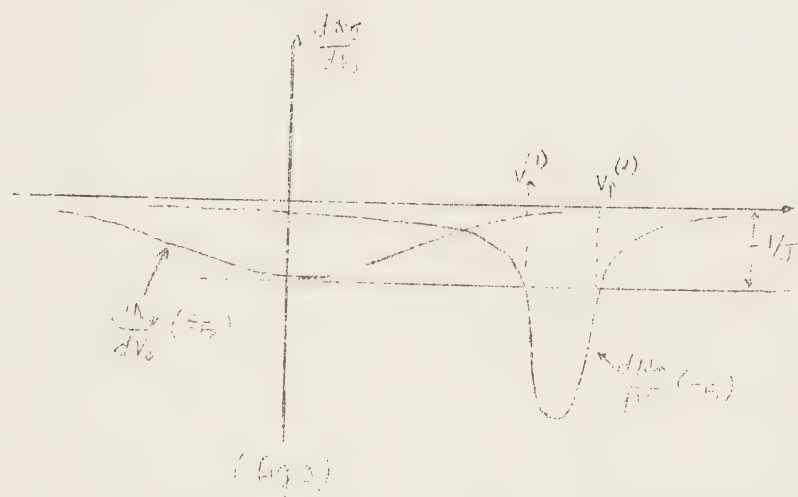
(fig 5)

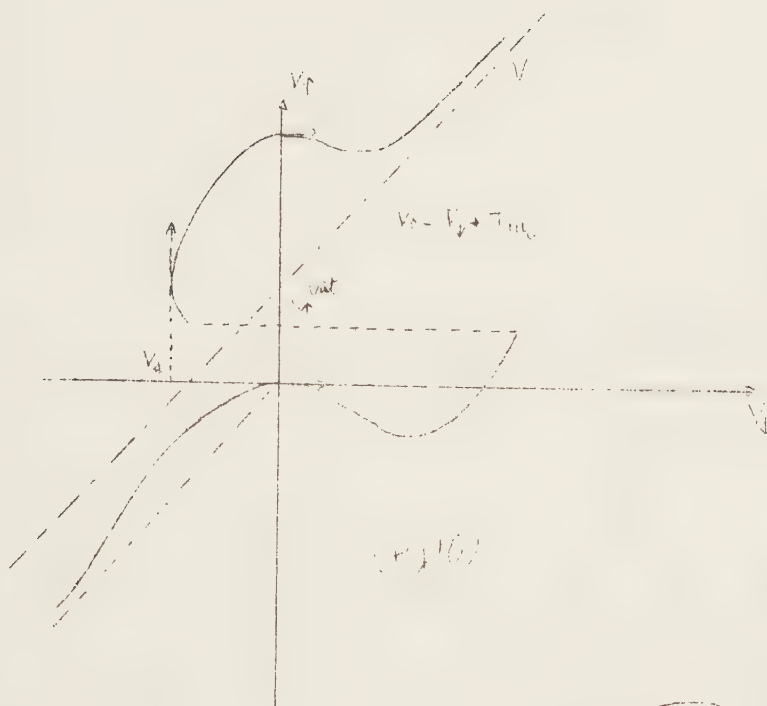


(fig 6)

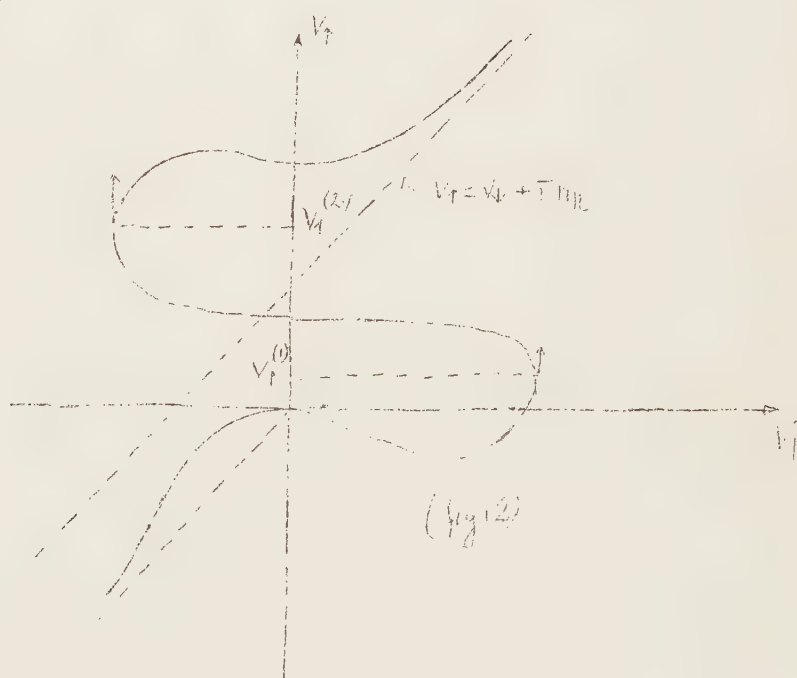


(fig 7)

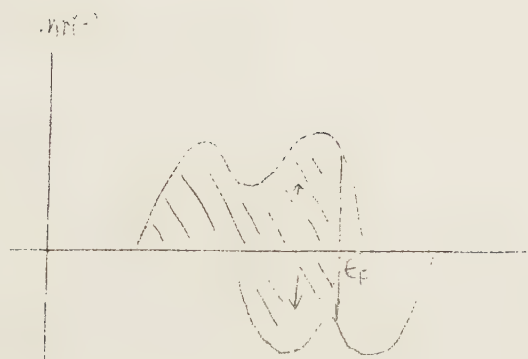




(fig 10)

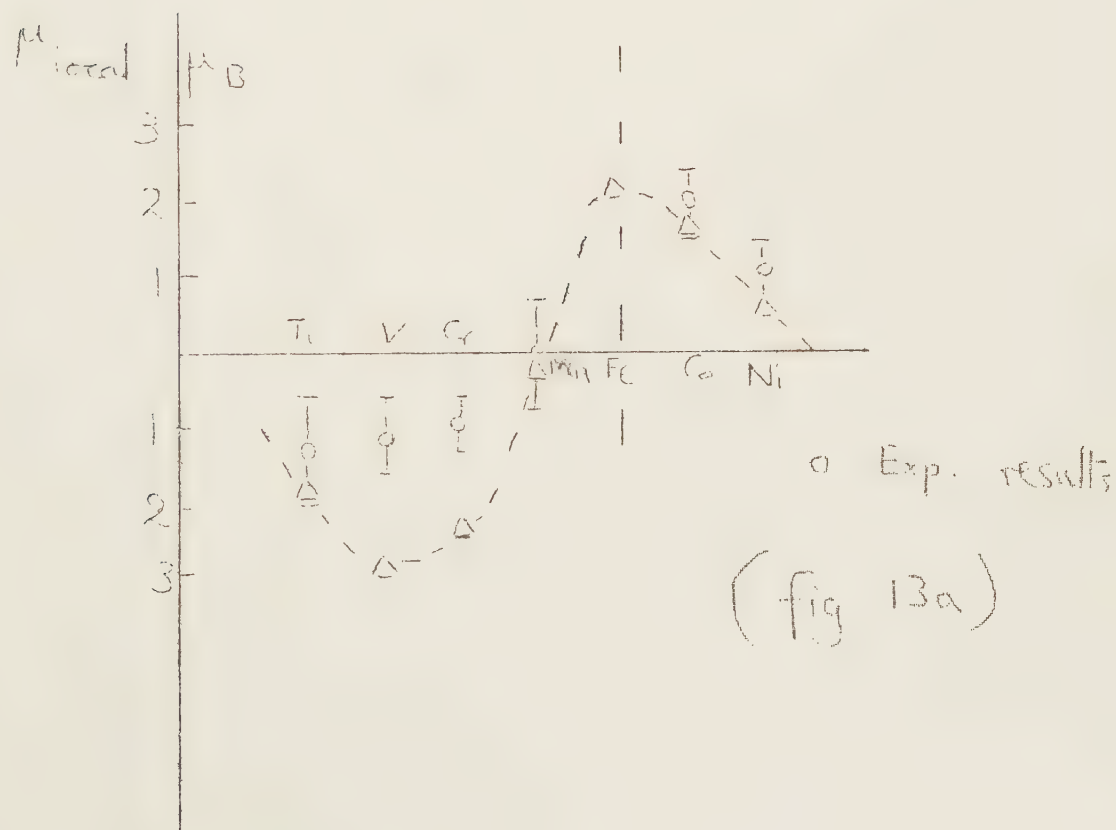
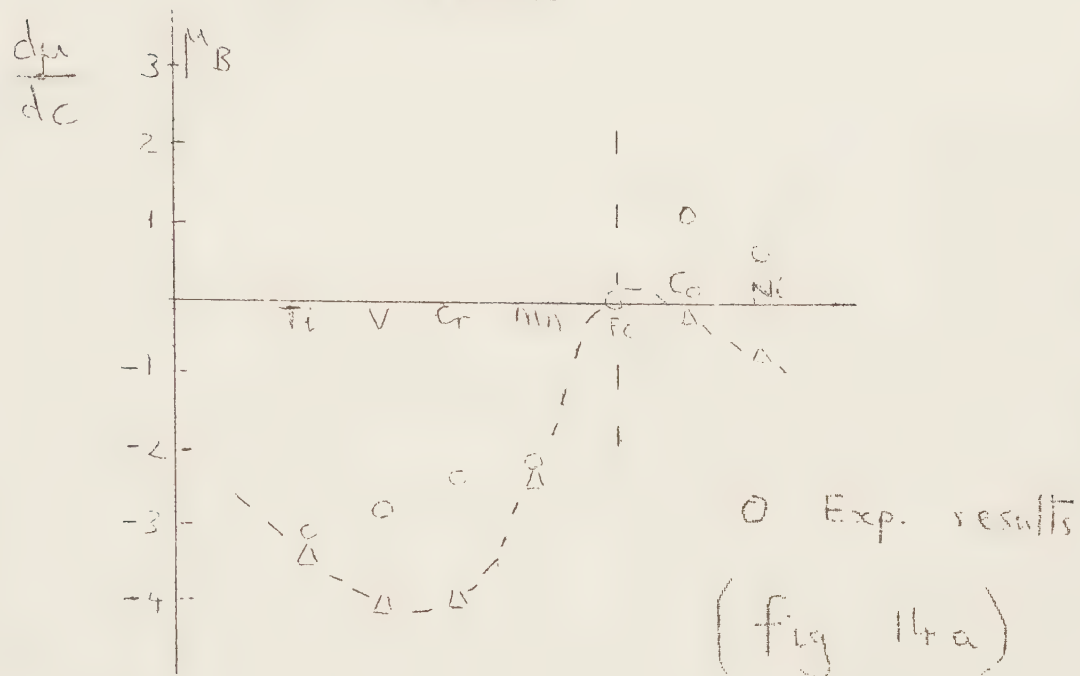


(fig 12)

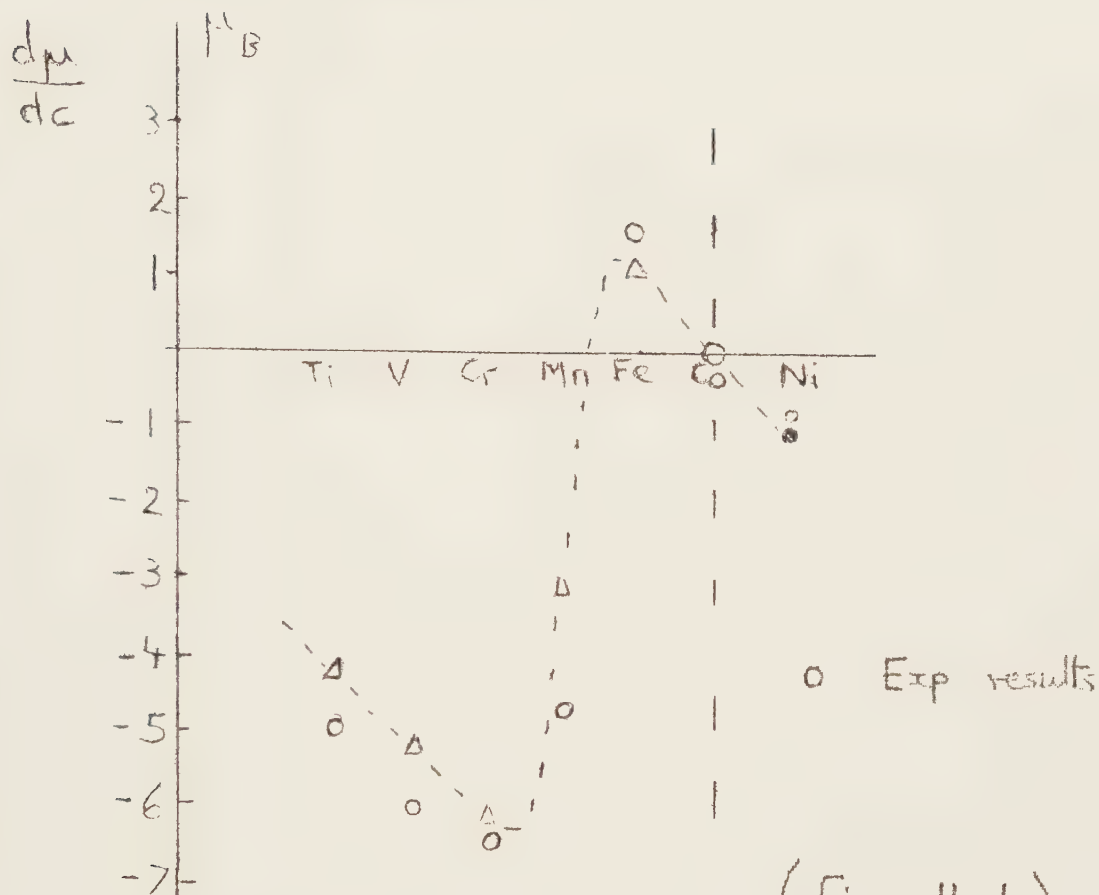


(fig 11)

Fe base

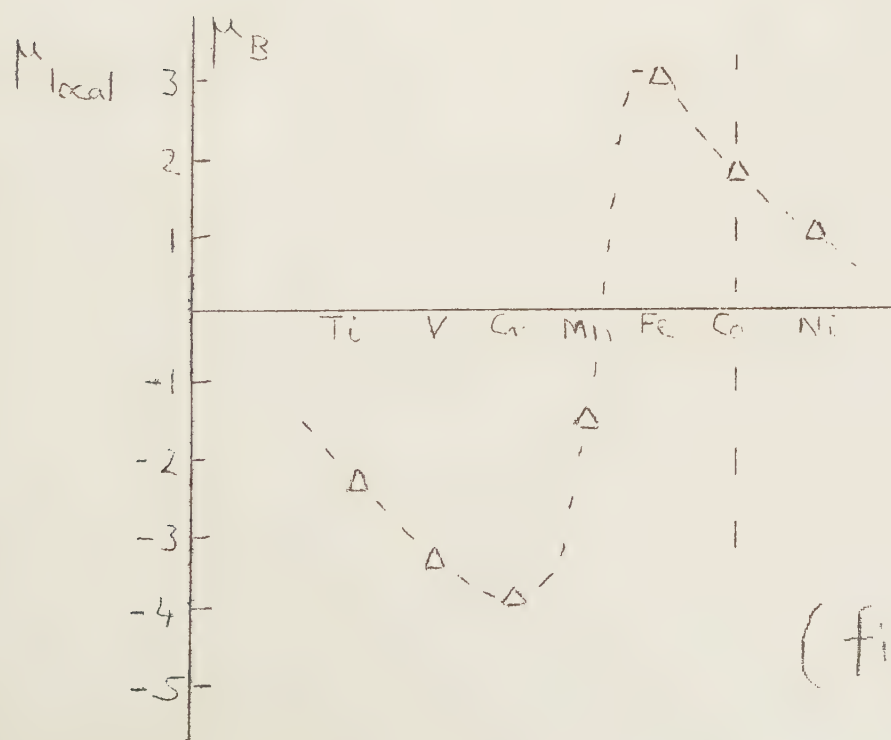


Co base



o Exp results

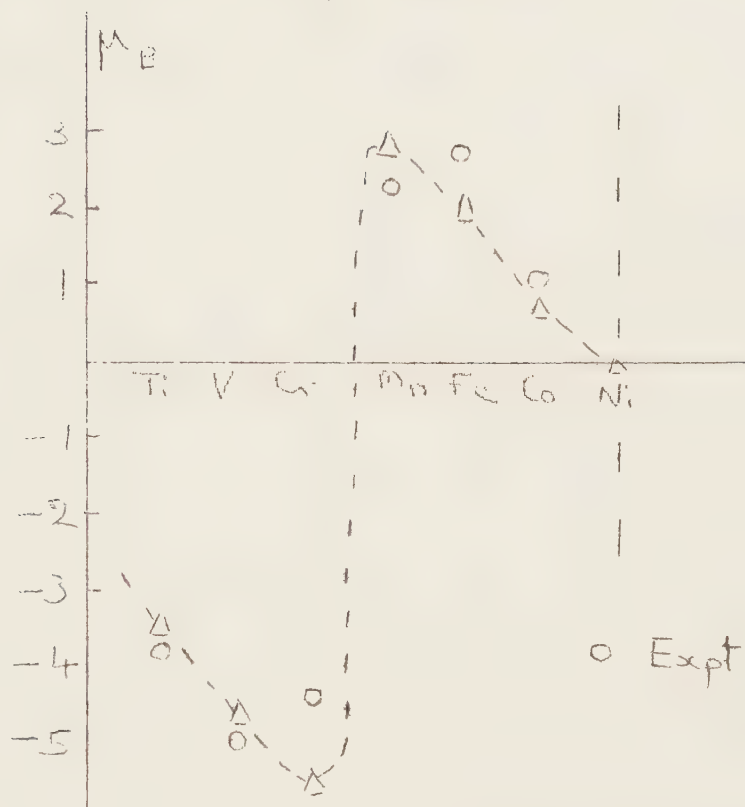
(fig 14b)



(fig 13b)

Ni base

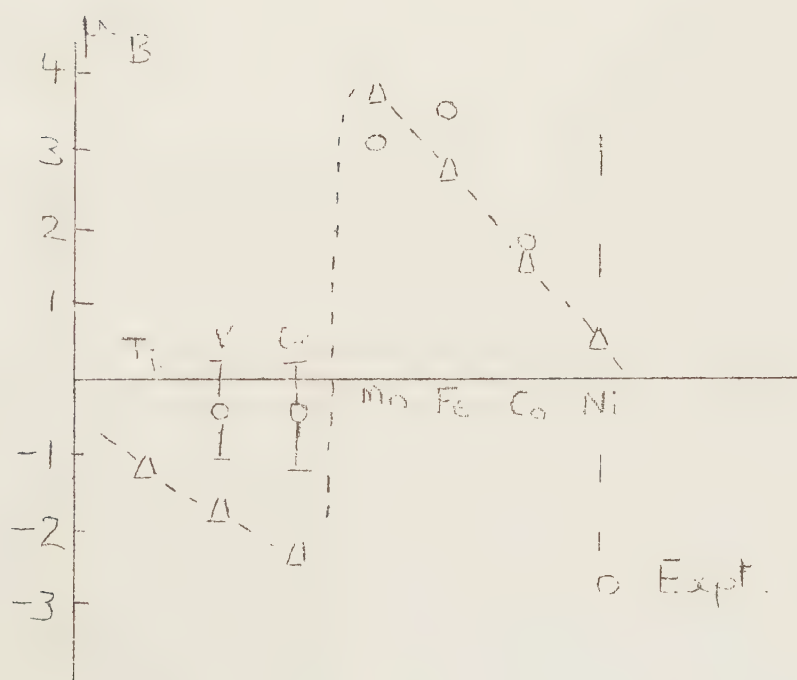
$\frac{d\mu}{dc}$



○ Expt. results

(fig 14c)

μ_{local}



○ Expt. results

(fig 13c)

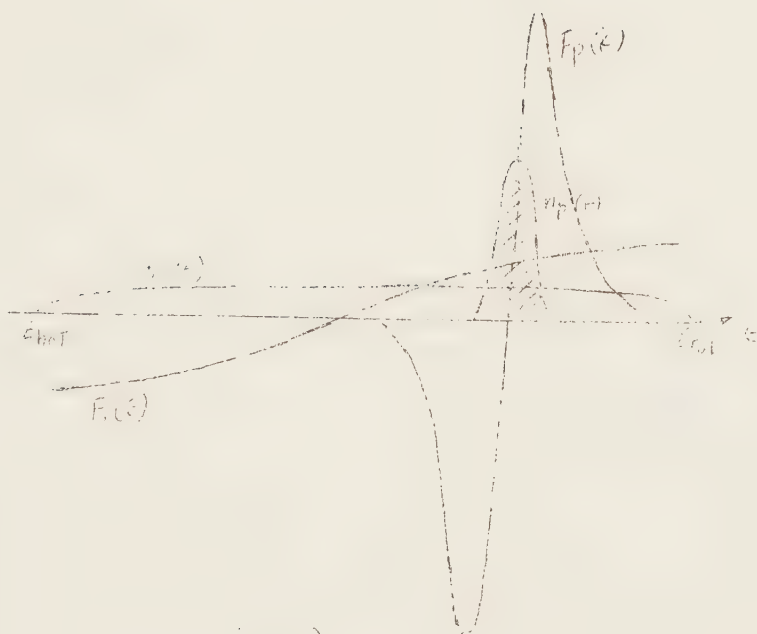


fig. 41)

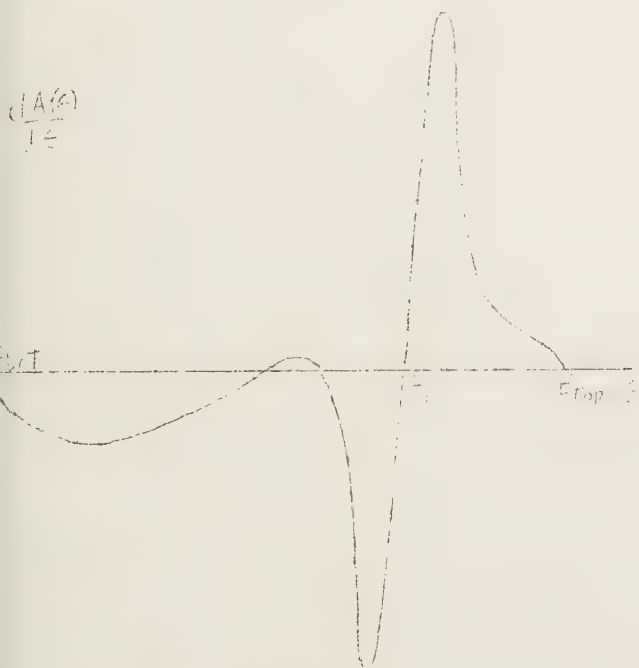


fig. A2

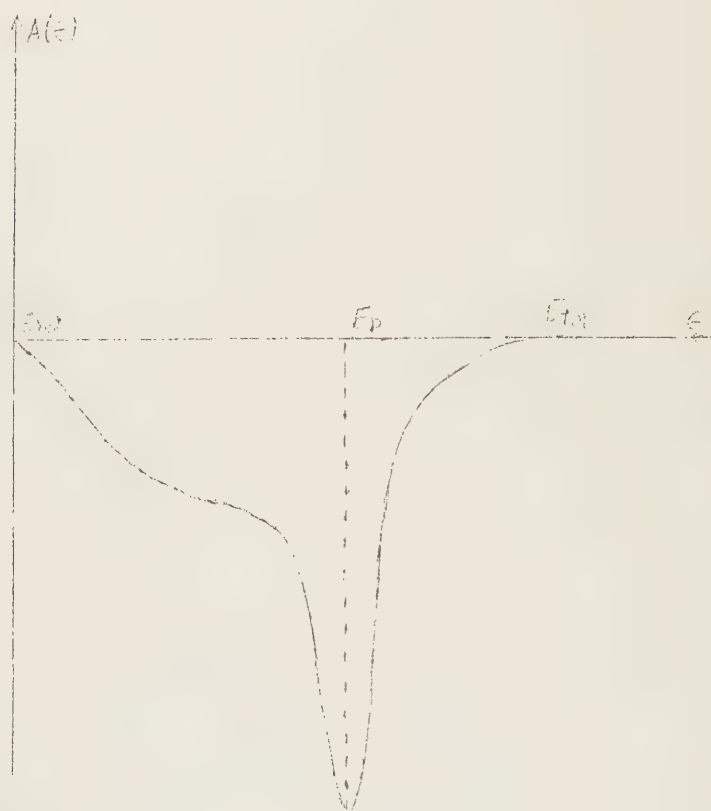


fig. A3

CHAPITRE III

CHANGEMENT DE RESISTIVITE INTRODUIT PAR LE MELANGE s-d INDUIT
PAR LES IMPURETES

Electronic structure of Iron based alloys

Electronic structure of Iron based alloys

by

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Abstract.

The Slater-Koster treatment of the impurity problem is extended in order to take into account the impurity induced interband scatterings in transition metals.

The simple picture adopted to describe the impurity atom and the host metal allows an exact solution of the scattering problem. The resistivity due to these transitions is then calculated.

An application is made to iron based alloys.

INTRODUCTION.

Transition metal alloys have been the subject of numerous studies in recent years, with special attention to the electronic structure.

The usually adopted band picture for the d electrons turns out to be quite useful to describe effects associated with the presence of an impurity, for instance, the redistribution of d electrons around it, and the change in averaged magnetic moment.

Recent measurements^{(1),(2)}, of resistivity and specific heat show a peculiar behaviour of metals of the first transitional series when dissolved in iron (Table IV, Fig.1).

The observed values of both quantities suggest that left hand impurities such as Mn and Cr produce in an iron lattice, effects that are far from simple perturbations as compared to those associated with Co and Ni.

In order to have a simple picture of the phenomena involved, we consider a band model for transition metals which consists of a broad conduction band, with low density of states which overlaps a narrow d-band.

According to Mott⁽³⁾, the resistivity of transition metals, comes mainly from transitions between the conduction band and the d-band, because of the high density of the states of the latter. If such a picture is adopted, the change in resistivity due to alloying is produced by impurity induced s-d transitions which are, roughly speaking, proportional to the change in d density of states.

As the screening effects are mostly produced in the d band, the above mechanism provides a simple connection between the resistivity and the d electronic structure.

On the other hand, in transition metals the d electrons are responsible for the specific heat ; then the changes in specific heat are also connected with the screening effects.

The observed change in the sign of the specific heat variation suggests, if the above picture is assumed, that when one goes from Mn to Cr and V one passes from a resonance phenomenon to an antiresonance phenomenon.

Resonance phenomena, discussed by Friedel and Wolff⁽⁴⁾⁽⁵⁾, are characterized by a high increase of state density, contrary to the anti-resonance where a high decrease is produced.

This interpretation is consistent with the resistivity data which shows a high value for Mn and a decrease when one goes to Cr and V.

For Co and Ni one has effects similar to perturbations, that means only a small negative variation of state density.

In the first paragraph of this paper, we describe the model for the impurity problem explaining the hypothesis on which is based. The second paragraph is an extension of the Slater-Koster treatment to a two band problem, the resistivity calculation being made in paragraph three. The rest of the papers concerns an application to iron based alloys.

§ 1 - Model for the two band impurity problem.

We divide this paragraph into two parts. The first one is a description of the impurity atom and of the scattering problem, the second being a simple discussion of the features associated with the host metal.

a-1) Description of the impurity atom.

The impurity atom is described by a perturbing potential $V(\underline{r})$, which is assumed to be both localized and spin independent.

Previous theoretical studies⁽⁶⁾ have indeed shown that the long-range oscillatory fringes of $V(\underline{r})$ are small compared to the central atomic part, provided that the Fermi surface has large enough cross section or if the density of states $n_d(E_F)$ is large enough. We assume that this result, obtained from a self-consistent perturbation approach is still qualitatively valid for our case.

These localized potentials can be shown theoretically to be fairly spin independent⁽⁷⁾ as long as the difference between the impurity and host atom exchange integrals is small, and the local change in magnetic moment is not too large.

For the sake of simplicity, we assume that this is true for the impurities considered.

a-2) Scattering problem.

The scattering problem can be divided into three parts :

- 1)- Scattering within the conduction band,
- 2)- Scattering within the d-band,
- 3)- Transition between the two bands (s-d mixing)

The corresponding matrix elements are :

$$\begin{aligned} V_{ss} &= \langle \phi_s(\underline{k}, \underline{r}) | V(\underline{r}) | \phi_s(\underline{k}', \underline{r}) \rangle \\ V_{dd} &= \langle \phi_d(\underline{k}, \underline{r}) | V(\underline{r}) | \phi_d(\underline{k}', \underline{r}) \rangle \\ V_{sd} &= \langle \phi_s(\underline{k}, \underline{r}) | V(\underline{r}) | \phi_d(\underline{k}', \underline{r}) \rangle \end{aligned}$$

ϕ_s and ϕ_{d_n} being the Bloch functions of the s-band and of the n-th d-sub-band respectively.

It can be shown, within the tight bonding approximation, and assuming a spherically symmetrical potential $V(r)$ that V_{dd} is independent of $\underline{k}$ and $\underline{k}'$, and of the d-sub-band.

For the V_{sd} matrix element we make the approximation that the same result is still valid.

Actually V_{sd} depends on $\underline{k}$ and $\underline{k}'$; thus our treatment of the s-d mixing effects is somewhat too crude.

The scattering processes described above produce the screening of the extra charge introduced by the impurity and the change in resistivity.

A simple perturbation argument (a better justification is given in § 2) shows the relative importance of the matrix elements involved.

The screening charge (up to second order in perturbation) can be written as :

$$Z(E_F) \approx -n_d(E_F) V_{dd} \left\{ 1 - \frac{V_{ss}}{V_{dd}} \frac{n_s(E_F)}{n_d(E_F)} \right\} - n_d(E_F) V_{dd}^2 F_d(E_F) \left\{ 1 + \frac{|V_{sd}|^2}{V_{dd}^2} \frac{n_s(E_F)}{n_d(E_F)} \right\} (1)$$

Where n_s and n_d are the state densities of the conduction and d-bands respectively,

$$F_d(E_F) = P \int \frac{n_d(\xi) d\xi}{E_F - \xi} \quad (P \text{ meaning the Cauchy principal value}) \text{ and } V_{ss} \approx V_{sd} \approx V_{dd}$$

Since for transition metals, $n_d(E_F) \gg n_s(E_F)$, the contributions of V_{ss} and V_{sd} to the screening charge may be neglected. V_{dd} can be determined, then in a phenomenological way by imposing $Z(E_F) = Z$, Z being the charge introduced by the impurity.

For the resistivity also, a perturbation treatment shows that the contributions of the several mechanisms are of the order of $|V_{sd}|^2 n_d$, $V_{dd}^2 n_d$, and $V_{ss}^2 n_s$.

Then, by the same argument as above, the term in V_{ss} may be neglected.

In a latter discussion (see appendix II) we give a more quantitative estimate of the importance of the remaining terms. It turns out that the V_{sd} terms are the dominant ones as far the resistivity is concerned.

In conclusion we can assume the screening to be mainly made in the d-band, and the resistivity change to be produced mostly by the impurity induced s-d mixing.

b) Adopted description of the host metal.

Different calculations have been made on the band structure of ferromagnetic transition metals⁽⁸⁾⁽¹¹⁾. These calculations are made either considering the

d-band independently from the conduction band⁽⁸⁾⁽⁹⁾, or taking into account the s-d mixing already existent in the host metal⁽¹⁰⁾⁽¹¹⁾. From⁽⁸⁾⁽⁹⁾, it turns out that the d-band can be treated satisfactorily within the tight-binding approximation, provided that one takes into account properly the degeneracy of the d-band.

A free electron approximation is then adopted for the conduction band.

Then, in the scattering problem discussed above one has to take into account the degeneracy of the d-band.

In recent papers,⁽⁷⁾⁽¹²⁾ Gautier and Kanamori discussed the scattering in a degenerate d-band.

They show by group-theoretical arguments that formally one still obtains the same results as in the non-degenerate case, provided that the usual state density $n_d(E)$ is replaced by the occupation function of the atomic orbitals, defined by :

$$n_d(E) = \frac{\Omega_0}{(2\pi)^3} \sum_n \int_{S_n(E)} \frac{|a_j^{(n)}(k)|^2 dS_k}{|E_k - E_n|} \quad , \quad \text{with} \quad \sum_i n_i(E) = n_d(E) \quad (2)$$

Ω_0 being the atomic volume, $E_k^{(n)}$ the usual dispersion relation and $\{a_i^{(n)}(k)\}$ the coefficients of the linear combinations defining the d-Bloch waves,

$$\Phi_n(k, r) = \sum_i \sum_{\lambda} a_{i\lambda}^{(n)}(k) e^{i k \cdot R_{i\lambda}} \psi_i(r - R_{i\lambda}) \quad .$$

Our approximation consists of (1) assuming in the d-band equal occupation of the Γ_{12} and Γ_{25} orbitals, which is equivalent to the assumption of a d-band made of 5 independent and equal subbands, and (2) considering a V_{sd} matrix element, that is independent of the d-orbital (spherical potential).

Such a proceeding enables us to give a simple solution of the complete scattering problem for the two band problem. The first assumption is only approximate, but justified by the fact that the width of the d-band seems to be large compared with the $\Gamma_{12} - \Gamma_{25}$ splitting⁽⁸⁾⁽⁹⁾.

The effects due to ferromagnetism of the host metal will be discussed in the application to iron alloys.

§ 2 - Extension of the Slater-Koster treatment for a two band problem.

In the part a) of this paragraph we present the solution of the scattering problem defined by the matrix elements V_{dd} and V_{sd} , which will be used in the calculation of the impurity resistivity, and discuss the physical meaning of the solution.

Part b) contains a more detailed discussion of the displaced charge. We discuss an expression for the screening charge that is valid even in presence of resonant effects in the d-band, provided that the s-d mixing effects are small. Details of the derivation of such expression are left for appendix 1.

a) Solution of the scattering problem.

The scattered wave function of the conduction electron can be expanded in terms of the complete orthonormal system formed by the functions $\phi_s(\mathbf{k}, \mathbf{r})$ and $\phi_d(\mathbf{k}, \mathbf{r})$ (the d-function being, as discussed in §1 non degenerate, tight binding functions)

$$\psi_s(\mathbf{k}, \sigma) = \phi_s(\mathbf{k}, \sigma) + \sum_{\mathbf{k}'_s} a_s(\mathbf{k}'_s, \sigma) \phi_s(\mathbf{k}'_s, \sigma) + \sum_{\mathbf{k}'_d} a_d(\mathbf{k}'_d, \sigma) \phi_d(\mathbf{k}'_d, \sigma) \quad (3)$$

where σ stands for the spin and the summations are extended to the s and d Brillouin zones respectively.

Such a wave function should satisfy

$$[H_0 + V(\mathbf{r})] \psi_s(\mathbf{k}, \sigma) = \epsilon_{\mathbf{k}\sigma} \psi_s(\mathbf{k}, \sigma) \quad (4)$$

H_0 being the monoatomic unperturbed Hamiltonian.

Substituting (3) into (4) and multiplying by s and d unperturbed functions, one gets a system of coupled equations that determines the coefficients $a_s(\mathbf{k}, \sigma)$ and $a_d(\mathbf{k}, \sigma)$. Such a system can be solved by the Green's function method ⁽⁵⁾ giving for (3)

$$\begin{aligned} \psi_s(\mathbf{k}, \sigma) = & \phi_s(\mathbf{k}, \sigma) + \frac{1}{N} \left\{ \frac{|V_{sd}|^2 G_d(\epsilon_{\mathbf{k}\sigma})}{1 - V_{dd} G_d(\epsilon_{\mathbf{k}\sigma}) - G_s(\epsilon_{\mathbf{k}\sigma}) G_d(\epsilon_{\mathbf{k}\sigma}) |V_{sd}|^2} \right. \\ & \sum_{\mathbf{k}'_s} \frac{\phi_s(\mathbf{k}'_s, \sigma)}{\epsilon_{\mathbf{k}\sigma} - \epsilon_{\mathbf{k}'_s\sigma} + i\eta} + \frac{1}{N} \left\{ \frac{V_{ds}}{1 - V_{dd} G_d(\epsilon_{\mathbf{k}\sigma}) - G_s(\epsilon_{\mathbf{k}\sigma}) G_d(\epsilon_{\mathbf{k}\sigma}) |V_{sd}|^2} \right\} \\ & \left. \sum_{\mathbf{k}'_d} \frac{\phi_d(\mathbf{k}'_d, \sigma)}{\epsilon_{\mathbf{k}\sigma} - \epsilon_{\mathbf{k}'_d\sigma} + i\eta} \right\} \quad (5) \end{aligned}$$

In this expression, $G_{i\sigma}(\epsilon_{\mathbf{k}\sigma})$ are the Green's function for this problem, defined by :

$$G_{i\sigma}(\epsilon_{\mathbf{k}\sigma}) = \frac{1}{N} \sum_{\mathbf{k}'_i} \frac{1}{\epsilon_{\mathbf{k}\sigma} - \epsilon_{\mathbf{k}'_i\sigma} + i\eta}, \quad i = s, d$$

and n being a small positive quantity that tends to zero.

Using the same technique one can solve for the scattered wave function of d-electron obtaining

$$\begin{aligned} \psi_d(\mathbf{k}, \sigma) = & \phi_d(\mathbf{k}, \sigma) + \frac{1}{N} \left\{ \frac{V_{dd} + V_{sd}^2 G_s(\xi_{\mathbf{k}\sigma})}{1 - V_{dd} G_d(\xi_{\mathbf{k}\sigma}) - G_s(\xi_{\mathbf{k}\sigma}) G_d(\xi_{\mathbf{k}\sigma}) |V_{sd}|^2} \right\} \sum_{\mathbf{k}'_d} \frac{\phi_d(\mathbf{k}'_d, \sigma)}{\xi_{\mathbf{k}\sigma} - \xi_{\mathbf{k}'_d, \sigma} + i\eta} \\ & + \frac{1}{N} \left\{ \frac{V_{sd}}{1 - V_{dd} G_d(\xi_{\mathbf{k}\sigma}) - G_s(\xi_{\mathbf{k}\sigma}) G_d(\xi_{\mathbf{k}\sigma}) |V_{sd}|^2} \right\} \sum_{\mathbf{k}'_s} \frac{\phi_s(\mathbf{k}'_s, \sigma)}{\xi_{\mathbf{k}\sigma} - \xi_{\mathbf{k}'_s, \sigma} + i\eta} \quad (6) \end{aligned}$$

A very simple physical picture can be given for the scattered terms in (5) and (6).

The second term of (5) describes the effect in the scattered wave of the s-s transitions via the d-band, this term being proportional to $|V_{sd}|^2$, while the third term contains the s-d transitions where the final state is a d-state. The second term of (5) is the only one present in the case of a transition impurity dissolved in a normal metal, the third one being a band effect which disappears when the d-band width tends to zero.

Expression (6) contains a term describing transitions within the d-band which is proportional to V_{dd} and two terms similar to the discussed above and describing d - d transitions via the s -band and d-s transition.

This expression reduces to the Slater-Koster result for a d-band if one makes $V_{sd} = 0$.

A simple interpretation can be given for the term

$$G_{s\sigma}(\xi_{\mathbf{k}\sigma}) G_{d\sigma}(\xi_{\mathbf{k}\sigma}) |V_{sd}|^2$$

which appears in all denominators. It corresponds to a broadening of the d levels by the s-d mixing. It can be shown that this term can be neglected for a broad d-band, but, on the contrary, it is the dominant one in very narrow band limit

b) Discussion of the displaced charge.

As discussed in § 1 the scattering mechanisms displace a certain amount of charge, which was shown in a rough way to be almost determined by d-band parameters and V_{dd} . Here we intend to discuss this problem in more detail.

The general expression⁽¹³⁾ for the displaced charge up to energy E is :

$$Z(E) = - \frac{1}{\pi} \text{trace } \pi \delta(E - H_0) K(E) \quad (7)$$

K(E) being the scattering operator defined by

$$K(E) = V(\mathcal{E}) + V(\mathcal{E}) \mathcal{P} \frac{1}{E - H_0} K(E),$$

the trace being calculated over the s and d functions.

The change in state density due to the impurity being given by

$$\Delta(E) = \frac{d}{dE} Z(E),$$

expression (7) enables a discussion of the variation of the specific heat, since it is proportional to $\int_0^E n(E) dE$.

1) Non degenerate d-band.

The scattering within the s-band can be neglected because of the above argument of the density of states ($n_s(E) \ll n_d(E)$) (8-1). One has then to consider the other two contributions. The evaluation of (7) can be made assuming the mixing effect to be small compared to the d-band scattering (some details of the calculation are given in appendix 1). One obtains then for the charge displaced up to the energy E

$$Z(E) \Rightarrow \frac{1}{\pi} \arctg \frac{V_{sd} n_d(E)}{1 - V_{dd} F_d(E)} + n_s(E) \frac{|V_{sd}|^2}{V_{dd}} \frac{1 - V_{dd} F_d(E)}{[1 - V_{dd} F_d(E)]^2 + [\pi V_{dd} n_d(E)]^2} + n_s(E) \frac{|V_{sd}|^2}{V_{dd}} \quad (8)$$

A simple physical meaning can be given to the terms present in this formula. The first term is the usual d-screening charge as derived by Wolff and Clogston⁽⁵⁾⁽¹⁴⁾ and corresponds to the scattering processes within the d-band. Then the same discussion by these authors which leads to the notion of virtual levels (resonant scattering) and of impurity bound states can be applied here.

In the application to iron alloys we discuss in more detail, for a concrete band structure, some features of these cases.

The two other terms in (8) correspond to the s-d mixing effect.

Essentially, the interband scattering mechanisms discussed before introduce in the scattered wave, say of a conduction electron, a certain d-character. In such a situation, each d-level will be broadened in energy and such a broadening will introduce a certain number of states below the Fermi level.

The second term of (8) corresponds to the total broadening of the extra d-states introduced by the perturbation. Such a term becomes zero exactly at resonance

($1 = V_{dd} F_d(E_F)$), a result that is easily understood if we take into account the symmetry of the "hump" in density of states introduced by the resonance.

The third term corresponds to the broadening of the state lying at the Fermi level,

2) Degenerate d-band.

As discussed in § 1-b) we take as an approximation for the d-band structure a model with five equal and independent subbands. In such a case, expression (8) is still valid for each subband provided that the density of states is replaced by $n_d(E)/5$ and consequently $F_d(E)$ by $F_d(E)/5$

$$Z(E) = \frac{5}{2i} \arctg \frac{V_{jd} n_d(E)/5}{1 - V_{dd} F_d(E)/5} + i s(E) \frac{|V_{sd}|^2}{V_{dd}} \frac{1 - V_{dd} F_d(E)/5}{[1 - V_{dd} F_d(E)/5]^2 + [V_{dd} n_d(E)/5]^2} + 5 n_s(E) \frac{|V_{sd}|^2}{V_{dd}} \quad (9)$$

§ 3 - Calculation of the change in resistivity due to impurities.

a) Relaxation time calculation.

We describe the resistivity of these alloys within a relaxation time approach⁽¹⁵⁾, extended for a two band problem. The usual model by Mott⁽³⁾ for the conductivity of transition metals is based on the hypothesis of a non-conducting d-band, all the current being carried by s-electrons.

Such a model, as suggested by the high effective mass ascribed to the d-electrons, is well confirmed by recent experiments⁽¹⁶⁾.

In the appendix II we give a highly simplified discussion of the two current problem and finally we estimate the ratio σ_d/σ_s , σ_s and σ_d being the conductivities associated to s and d electrons respectively.

It turns out that $\sigma_d/\sigma_s = 20\%$ in good agreement with Cole's results⁽¹⁶⁾ for Pd Ag and Pd Rh.

Qualitatively, if the current is only due to conduction electrons, one should expect two terms contributing to the resistivity.

1) The s-s transitions via the d-band, which is the only present in the case of an isolated d-state mixed to a conduction band (for instance in the case of normal metals with transition impurities).

2) The s-d transitions, where the final state of the scattered electron is a d-state. Such a term is a pure band effect, reflecting the itinerant character of d-electrons. For a zero band width this term disappears.

These two contributions are derived in the Appendix II from Boltzman's equation in the approximation of V_{sd} independent of $\underline{k}$ and $\underline{k}'$.

If such a picture is adopted, the relaxation time is :

$$\frac{1}{\tau_{ss}} = \int \left\{ 1 - \frac{(\partial E_{ss} / \partial k_x^s) k'_s}{(\partial E_{ss} / \partial k_x^s) k_s} \right\} P_{ss}^{\sigma}(\underline{k}_s, \underline{k}'_s) dS_{\underline{k}'_s} + \int P_{sd}^{\sigma}(\underline{k}_s, \underline{k}'_d) dS_{\underline{k}'_d} \quad (10)$$

$P_{si}^{\sigma}(\underline{k}, \underline{k}'_i) dS_{\underline{k}'_i}$ is the transition probability per unit time that a conduction electron of spin σ jumps into the i -th band by the mechanisms described above.

These transition probabilities can be calculated from the usual formula

$$P_{si}^{\sigma}(\underline{k}, \underline{k}'_i) dS_{\underline{k}'_i} = \frac{2\pi}{(2\pi)^2 \hbar} \int d\varepsilon_{\underline{k}'_i} \delta(\varepsilon_{\underline{k}s} - \varepsilon_{\underline{k}'_i\sigma}) |\langle \phi_i(\underline{k}'_i, \sigma) | V(\underline{r}) | \psi_s(\underline{k}, \sigma) \rangle|^2 \frac{dS_{\underline{k}'_i}}{|\nabla_{\underline{k}'_i} \varepsilon_{\underline{k}'_i\sigma}|} \quad (11)$$

$\psi_s(\underline{k})$ being the scattered function as calculated in (§ 2) and $\phi_i(\underline{k}')$ the i -th band unperturbed function.

Expressions (10) and (11) are valid in general, independent of any assumption for the s and d bands. With a free electron approximation for the conduction band and if V_{dd} and V_{sd} are $\underline{k}$ independent, one obtains for $\tau_{s\sigma}$:

$$\frac{1}{\tau_{s\sigma}} = \frac{1}{2\hbar} |\langle \phi_s | V(\underline{r}) | \psi_s \rangle|^2 n_{s\sigma}(\varepsilon_{\underline{k}s}) \int (1 - \cos\theta) \sin\theta d\theta d\varphi + \frac{2\pi}{\hbar} |\langle \phi_d | V(\underline{r}) | \psi_s \rangle|^2 n_{d\sigma}(\varepsilon_{\underline{k}\sigma}) \quad (12)$$

where θ is the angle between $\underline{k}'$ and $\underline{k}$.

With the matrix elements calculated using the wave function (5), this becomes

$$\frac{1}{\tau_{s\sigma}} = \frac{2\pi}{\hbar} \left\{ \frac{|V_{sd}|^4 |G_{d\sigma}(\varepsilon_{\underline{k}\sigma})|^2 n_{s\sigma}(\varepsilon_{\underline{k}\sigma}) + |V_{sd}|^2 n_{d\sigma}(\varepsilon_{\underline{k}\sigma})}{|1 - V_{dd} G_{d\sigma}(\varepsilon_{\underline{k}\sigma}) - G_{s\sigma}(\varepsilon_{\underline{k}\sigma}) G_{d\sigma}(\varepsilon_{\underline{k}\sigma})| |V_{sd}|^2} \right\} \quad (13 a)$$

We emphasize that due to the approximation V_{dd} and V_{sd} independent of $\underline{k}$ and $\underline{k}'$, the relaxation time and, consequently, the resistivity are independent of the topology of the d energy surfaces, the only d band parameter involved being the density of states. The relaxation time given by (13 a), calculated for non-degenerate bands, must be modified in order to take into account the degeneracy of the d -band.

Making use of the approximation (§ 1) of a d band made of five equal and independent subbands, the contribution of each sub-band is obtained from (13 a) replacing

$n_{ds}(\xi_{k\sigma})$ and $G_{ds}(\xi_{k\sigma})$ by $n_d(\xi_{k\sigma})/5$ and $G_d(\xi_{k\sigma})/5$ respectively.

The total contribution of the d-subbands to the relaxation time is given by 5 times the contribution of each subband separately, that means :

$$\frac{1}{G_{sr}} = \frac{2\pi}{h N} \left\{ \frac{5|V_{sd}|^4 |G_{ds}(\xi_{k\sigma})/5|^2 n_{ss}(\xi_{k\sigma}) + |V_{sd}|^2 n_{ds}(\xi_{k\sigma})}{\left| 1 - V_{dd} G_{ds}(\xi_{k\sigma})/5 - G_{ss}(\xi_{k\sigma}) G_{ds}(\xi_{k\sigma}) |V_{sd}|^2/5 \right|^2} \right\} \quad (13 b)$$

b) Change in resistivity due to impurities.

Now we consider the case of ferromagnetic transition alloys.

At low temperatures, the main contribution to the resistivity of the host metal comes from the scattering of electrons by spin waves. In the case of the alloys we consider a temperature range where the important effects are the impurity scattering and the spin wave scattering.

It will be assumed that in this temperature range the mean free path due to collisions with the impurities is much bigger than that corresponding to spin waves.

In this case, due to collisions with magnons, the electrons will change of spin many times before colliding with an impurity. Then, as far the impurity is concerned, the electron has equal chance of having $\uparrow$ or $\downarrow$ spin. This introduces a change in resistivity given by :

$$\Delta \rho \approx \frac{1}{2} (\rho_{i\uparrow} + \rho_{i\downarrow}) \quad (14)$$

$\rho_{i\sigma}$ being the resistivity calculated from G_{sr} (13 b).

In the classical way one obtains from (14) and (13)

$$\Delta \rho \approx \frac{2\pi h c}{c^2 h N_a} \sum_{\sigma} \left\{ \frac{5|V_{sd}|^4 |G_{ds}(E_F)/5|^2 n_s(E_F) + |V_{sd}|^2 n_d(E_F)}{\left| 1 - V_{dd} F_{ds}(E_F)/5 - G_{ss}(E_F) G_{ds}(E_F) |V_{sd}|^2/5 \right|^2} \right\} \quad (15)$$

N_a being the number of atoms p/unit volume, the concentration c appearing as a result of the approximation independent scatterings.

Now, because $n_s(E_F) \ll n_d(E_F)$, the broadening effect in the denominator may be neglected, giving then :

$$\Delta \rho \approx \frac{2\pi h c}{c^2 h N_a} \sum_{\sigma} \left\{ \frac{5|V_{sd}|^4 |G_{ds}(E_F)/5|^2 n_{ss}(E_F) + |V_{sd}|^2 n_{ds}(E_F)}{\left[1 - V_{dd} F_{ds}(E_F)/5 \right]^2 + \left[V_{dd} n_{ds}(E_F)/5 \right]^2} \right\} \quad (16)$$

§ 4 - Application to iron based alloys.

In this paragraph, we apply to iron based alloys the model developed before.

B.C.C. transition metals present a pronounced minimum in the state density curve, which is the only d-band parameter involved in our model.

Then, one has to find a simple picture for the band structure of iron, that takes account properly of such a minimum.

a) Band model for iron.

The ferromagnetism shown by the d electrons in iron, will be described by a simple band picture, where, owing to exchange, the $\uparrow$ spin subband is displaced in energy relative to the $\downarrow$ spin one.

We chose a simple form for the spin subbands, which consists of two similar overlapping parabolae. Such a model presents the advantage of a simple analytical form (which enables the calculation of $F_d(E)$), and exhibits the pronounced minimum required by the b.c.c. structure (Fig.2).

The only parameters involved are: the width of the parabolae, their maximum value, and the width of their overlap.

A possible way of determining these factors is to require that each spin subband contains 5 states p/atom, use the experimental value of the magnetic moment; and assume the usual value of 2.5 electrons for the occupation of the $\downarrow$ spin subband.

The results of such a procedure are shown in Table I

TABLE I

	Band width (eV)	Specific heat (cal/mol °K) $\times 10^{-4}$
model	4.7	8
exp. or calc.	4 to 6	12

b) Qualitative discussion of these alloys.

We discuss now, for the particular band picture adopted, the charge displaced by the potential $V(r)$.

Such a discussion is divided in two parts : first we estimate roughly the contribution of the s-d mixing effect and then, we discuss the behavior of the charge displaced in the d band, $Z_d(E)$, as a function of E, for several values of V_{dd} . The relation

$$\Delta n_d = \frac{dZ_d}{dE}$$

is then used to relate the changes in state density to the previous discussion, and leads to a qualitative understanding of the change in resistivity and specific heat.

1) s-d mixing contribution.

In paragraph 2b) and appendix I, an expression is given for the total displaced charge by $V(x)$.

The d-band parameters involved $n_d(E_F)$ and $F_d(E_F)$ are calculated from the band picture adopted above. The most difficult parameter to be estimated is the strength of the impurity s-d mixing.

Failing a reliable self-consistent Hartree or Hartree-Fock calculation, we consider V_{sd} as a parameter to be chosed in order to get agreement with the resistivity experimental data.

Any way, and order of magnitude of V_{sd} may be obtained from a band calculation in which s-d mixing is taken into account⁽¹⁰⁾. It turns out that in pure iron $V_{sd} \approx 1$ eV.

In table II we give for three values of V_{sd} , the ratio Z_{sd}/Z_d for several values of V_{dd}

TABLE II

V_{dd} (ev)	$V_{sd} = 0.8$ (ev)	$V_{sd} = 0.7$ (ev)	$V_{sd} = 0.6$ (ev)
0.5	13%	10%	7%
0.6	4%	3%	2%
0.7	- 2%	-1.5%	- 1%
0.9	- 8%	-6.5%	- 5%
1.2	- 10%	-8%	- 6%
1.5	- 9%	-7%	-5%

These results suggest the picture of a pure d-band screening, at least in the adopted range of values of V_{sd} and V_{dd} . If we take such a picture, we can determine for each alloy the value of V_{dd} using :

$$Z(E_F) = Z_d(E_F) \quad \text{with}$$

$$Z_d(E) = -\frac{5}{\pi} \arctg \frac{\pi V_{dd} n_d(E)/5}{1 - V_{dd} F_d(E)/5} \quad (17)$$

The results of such a procedure are listed in Table III.

TABLE III

Alloy	V_{dd} (eV)	Total change displaced
Fe Co	- 1.1	+ 1
Fe Mn	+ 0.5	- 1
Fe Cr	+ 0.9	- 2
Fe V	+ 1.5	- 3

2) Qualitative discussion of the changes in d-state density.

We discuss first the behaviour of (17) as a function of energy, for several values of V_{dd} , restricting ourselves for the moment to repulsive impurities.

For very small V_{dd} , (17) can be written approximately as $Z_d(E) = -V_{dd} n_d(E)$. In this limit, $Z_d(E)$ has the same shape as the state density curve, but with opposite sign (Fig.3). Now we consider the first solution of the equation $1 - V_{dd} F_d(E)/5 = 0$ which occurs for $V_{dd} = 1.1$ eV, at $E = E_0$, E_0 being the corresponding energy of the maximum of the function $F_d(E)$ (Fig.2). The behaviour of $Z_d(E)$ in the interval between the small potential limit and $V_{dd} = 1.1$ eV can be described as follows.

Starting from zero, at the top of the band, $Z_d(E)$ decreases to a certain minimum value, this minimum increasing in absolute value with V_{dd} , and then increases, having after that a similar behaviour to the small perturbation limit (Fig.4 and 5):

For $V_{dd} = 1.1$ eV one still has the same trend of curve, but the minimum value now is -2.5 , which corresponds to the infinite argument of the arctangent (Fig.5).

If one proceeds increasing V_{dd} , one arrives to extract a bound state from the band, the critical potential for that being $V_c = 5/F_d(E_{nv})$.

For our case $V_c = 1.3$ eV, and in the interval $1.1 \leq V_{dd} \leq 1.3$, one still has the same behaviour shown in Fig. 5, but with a minimum which is in absolute value somewhat larger than 2.5 . When the bound state is extracted, the behaviour of $Z_d(E)$ changes completely (Fig.6), starting from -5 at the top of the band, and then increasing having after that the same behaviour as in the previous cases.

From the above discussion, we can derive the behaviour of the change in state density at the $\uparrow$ spin Fermi level, given by $\Delta n_{\uparrow}(E_{F\uparrow}) = \left(\frac{d Z_d}{d E}\right)_{E_{F\uparrow}}$.

For $V_{dd} < V_c$, fig. 3,4,5 show that $\Delta n_{\uparrow}(E_{F\uparrow})$ increases from small values in the small potential limit to a rather big value, decreasing then to attain negative values when one approaches $V_{dd} = V_c$. This particular behaviour is connected with the fact that the $\uparrow$ spin Fermi level is lower than the energy corresponding to the maximum of $F_d(E)$.

One passes then from a resonant scattering to the beginning of an antiresonance when V_{dd} passes from 0 to V_c . For $V_{dd} > V_c$, a high negative slope is observed, characterizing an antiresonant process.

From this discussion and Table III we can understand the different behaviour of the several impurities.

For Mn case ($V_{dd} = 0.5$) one lies in the first part of the interval $V_{dd} = 0$ to $V_{dd} = 1.1$, which corresponds to a resonant scattering, then a positive and rather large change of state density is produced at the Fermi level.

Cr is a somewhat intermediate case, ($V_{dd} = 0.9$), which corresponds to the beginning of anti-resonance.

Finally, V case ($V_{dd} = 1.5$) lies in the antiresonant region, where a large negative change is observed.

Up to here only the behaviour at the $\uparrow$ spin Fermi level was discussed. Since the band is symmetric with respect to the $\downarrow$ spin Fermi level, $F_d(E)$ is an anti-symmetric function which is zero at this point.

In such a situation, $Z_d(E)$ is an increasing function of energy around the middle of the band, and the positive slope increases with increasing V_{dd} , for all the values of V_{dd} .

Then, as far $\downarrow$ spins are concerned, all the impurities have a similar behaviour:

Finally, for attractive impurities, due to the antisymmetry of $F_d(E)$ the

behaviour of $Z_d(E)$ can be obtained from the repulsive case only by interchanging the two halves of the band, and changing the sign of the displaced charge. Then for Co case, ($V_{dd} = -1.1$), near the spin Fermi level, one has the same shape of curve as one had near the bottom of the band for $V_{dd} = +1.1$, which corresponds to a small negative change in state density.

c) Specific heat and resistivity of these alloys.

The change per unit concentration of impurities of the low temperature specific heat is given by :

$$\Delta\chi = \frac{1}{3} \pi^2 k^2 \Delta n_d(E_F) \quad (18)$$

k being Boltzman's constant, and $\Delta n_d(E_F)$ being total change in state density at the Fermi level.

$\Delta n_d(E_F)$ can be calculated from expression (17), giving for $\Delta\chi$:

$$\Delta\chi = \frac{1}{3} \pi^2 k^2 v_{dd}^2 \sum_{\sigma} n_{d\sigma}(E_F)/5 \left\{ \frac{\left[\cotg \pi Z_d(E_F)/5 \right] \left(\frac{d n_{d\sigma}}{dE} \right)_{E_F} - \left(\frac{d F_{d\sigma}}{dE} \right)_{E_F}}{\left[1 - V_{dd} F_{d\sigma}(E_F)/5 \right]^2 + \left[\pi V_{dd} n_{d\sigma}(E_F)/5 \right]^2} \right\} \quad (19)$$

The results of the numerical evaluation of (19) are given in the Table IV.

TABLE IV

Alloy	$n_d(E_F)$ (States/eV atom)	$^{th}(\text{Cal/Mol } ^\circ K^2) \times 10^{-4}$	$^{obs}(\text{Arrot})^{(2)}$
Fe Mn	+ 0.46	2.5	5.4
Fe Cr	- 0.12	- 0.66	- 5.0
Fe V	- 0.45	- 2.5	- 5.0

Table IV confirms the qualitative discussion of the preceding paragraph, showing the predominance of antiresonant scattering in Cr and V, and a resonant scattering for Mn case.

As far as the resistivity is concerned, expression (16) was evaluated numerically for three values of $|V_{sd}|$. The obtained results are shown in Fig. (1). It turns out that for $|V_{sd}| \approx 0.7$ eV one gets a rather good agreement with experimental

results.

In table IV, using $|V_{sd}| = 0.7$ eV, we give the separate contributions of the two spin directions to the scattering mechanisms : s-s scattering via d-band and s-d scattering.

TABLE V

Alloy	$\Delta\rho_{ss}^{\uparrow}$	$\Delta\rho_{sd}^{\uparrow}$	ss	sd
Fe Mn	1.03	4.55	0.01	0.57
Fe Cr	1.00	4.25	0.01	0.55
Fe V	0.44	1.90	0.01	0.54
Fe Co	0.14	0.64	0.02	0.62

The relative importance of the mechanism producing the resistivity can be seen in Table V (the unities are micro - ohm cm/%).

Comparing the results for Mn and Co, we see clearly the effect of resonance in the resistivity produced in the spin band. At the same time comparison between Mn, Cr and V alloys shows the predominance of the antiresonance when one passes from Mn to V, as was already seen in the case of specific heat.

Conclusion.

This simple picture in which the electronic structure of the d-band plays the essential role turns out to explain qualitatively the available experimental results.

The opposite behaviour of the change in d-state density in resonant and anti-resonant limits explains the sign of the change in low temperature specific heat, and the decrease of resistivity for repulsive impurities.

The different behaviour of Fe Mn and Fe Co turns out to be explained by the absence in Co case of a resonant scattering, present in Mn case.

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APPENDIX I

The displaced charge can be written as

$$Z(E) = - \frac{1}{\pi} \sum_{m=1}^{\infty} A_m \text{trace } x^m \quad (\text{A.1})$$

where $x = \pi \delta(E - H_0) K(E)$ and $\text{trace } x^m = \sum_{k_s} \langle k_s | x^m | k_s \rangle + \sum_{k_d} \langle k_d | x^m | k_d \rangle$

Since the unity operator for this problem is $\sum_{k_s} |k_s\rangle \langle k_s| + \sum_{k_d} |k_d\rangle \langle k_d| = 1$,

the calculation of the trace involves the calculation of $\langle k_i | x | k_j \rangle$, $i, j = s, d$.

Taking into account $n_s(E) \ll n_d(E)$ one obtains :

$$\langle k_s | x | k_s \rangle \approx \frac{\pi \delta(E - \epsilon_{k_s}) |V_{sd}|^2 F_d(E)}{1 - V_{dd} F_d(E)}$$

$$\langle k_d | x | k_d \rangle \approx \frac{\pi \delta(E - \epsilon_{k_d}) V_{dd}}{1 - V_{dd} F_d(E)} \quad (\text{A.2})$$

$$\langle k_s | x | k_d \rangle \approx \frac{\pi \delta(E - \epsilon_{k_s}) |V_{sd}|^2}{1 - V_{dd} F_d(E)}$$

$$\langle k_d | x | k_s \rangle \approx \frac{\pi \delta(E - \epsilon_{k_d}) |V_{sd}|^2}{1 - V_{dd} F_d(E)}$$

trace x^m is then calculated using (A.2) and the approximation that V_{sd} is enough small to neglect powers superior to 2. One gets :

$$\text{trace } x^m \approx \left[\frac{\pi n_d(E) V_{dd}}{1 - V_{dd} F_d(E)} \right]^m + \frac{n_s(E) |V_{sd}|^2}{V_{dd} [1 - V_{dd} F_d(E)]} \times m \left[\frac{\pi n_d(E) V_{dd}}{1 - V_{dd} F_d(E)} \right]^{m-1} \quad \text{for } m \neq 1 \quad (\text{A.3})$$

$$\text{and trace } x \approx \frac{n_d(E) V_{dd}}{1 - V_{dd} F_d(E)} + \frac{n_s(E) |V_{sd}|^2 F_d(E)}{1 - V_{dd} F_d(E)}$$

Expression (A.3) substituted in (A.1) leads to formula (8) of the text.

APPENDIX II

Two currents problem

In this appendix we extend the usual relaxation time calculation⁽¹⁵⁾ to a two band problem. For that we introduce the d and s Fermi-Dirac distribution functions $f_d(k_d)$ and $f_s(k_s)$ in presence of an electric field and $f_d^0(k_d)$, $f_s^0(k_s)$ in the absence of it;

Assuming the applied field parallel to the x-axis one has :

$$f_i(k_i) = f_i^0(k_x^i - \frac{eE}{\hbar}t; k_y^i; k_z^i) \quad (B.1), \quad i = s, d$$

From (B.1) one calculates the time rate of change of the distribution functions due to the external field

$$\left(\frac{df_i(k_i)}{dt} \right)_{\text{field}} = - \frac{eE}{\hbar} \frac{df_i}{dE_i} \frac{\partial E_i}{\partial k_x^i} \quad (B.2)$$

then, due to the external fields, the distributions will shift, in a rate given by (B.2) until the effect of the field is exactly balanced by the collision processes, defining then the relaxation times τ_s and τ_d . In such a situation, the distribution functions are given by :

$$f_i(k_i) = f_i^0(k_i) - \frac{eE}{\hbar} \frac{df_i}{dE_i} \frac{\partial E_i}{\partial k_x^i} \tau_i \quad (B.3)$$

In order to determine τ_i one has to calculate the rate of change due to collisions and then impose the steady state condition

$$\left(\frac{df_i(k_i)}{dt} \right)_{\text{field}} = - \left(\frac{df_i(k_i)}{dt} \right)_{\text{collisions}}$$

The number of i electrons in the volume element $d k_i$ being given by $\frac{d k_i}{(2\pi)^3} f_i(k_i)$, the time rate of jumps outside this volume element is :

$$\frac{d k_i}{(2\pi)^3} f_i(k_i) \left[\int_{S_i(E_i)} [1 - f_i(k'_i)] P_{ii}(k_i, k'_i) dS_{k'_i} + \int_{S_j(E_i)} [1 - f_j(k'_j)] P_{ji}(k_i, k'_j) dS_{k'_j} \right] \quad i \neq j \quad (B.4)$$

where $P_{ji}(k_i, k'_j)$, $i, j = s, d$, is the transition probability per unit time that an i -th band electron is scattered into the j -th band.

Similarly, the time rate of jumps into the volume element is :

$$\frac{d k_i}{(2\pi)^3} \left[1 - f_i(k_i) \right] \left\{ \int_{S_i(E_i)} P_{ii}(k'_i, k_i) f_i(k'_i) dS_{k'_i} + \int_{S_j(E_i)} P_{ij}(k'_j, k_i) f_j(k'_j) dS_{k'_j} \right\} \quad i \neq j \quad (B.5)$$

Then, $\left(\frac{d f_i(k_i)}{dt} \right)_{\text{collisions}}$ is given by the difference between (B.4) and (B.5).

Substituting in (B.4) and (B.5), $f_i(k_i)$ and $f_j(k_j)$ by the expressions (B.3), and using the steady state condition, one obtains for the relaxation times system of coupled equations :

$$A_{ii} \zeta_i(E_F) + A_{ij} \zeta_j(E_F) = 1 \quad (i \neq j)$$

$$A_{ii} = \int_{S_i(E_F)} \left[1 - \frac{(\partial E_i / \partial k_x^i) k'_i}{(\partial E_i / \partial k_x^i) k_i} P_{ii}(k_i, k'_i) dS_{k'_i} + \int_{S_j(E_F)} P_{ji}(k_i, k'_j) dS_{k'_j} \right] \quad (B.6)$$

$$A_{ij} = - \frac{\frac{d f_j^0}{d E_j} \int_{S_j(E_F)} \left(\frac{\partial E_j}{\partial k_x^j} \right) P_{ij}(k_i, k'_j) dS_{k'_j}}{\left(\frac{\partial E_i}{\partial k_x^i} \right) k_i \frac{d f_i^0}{d E_i}}$$

For the particular case where the matrix element $V_{ij} = \langle \phi_i(k_i) | V(r) | \phi_j(k_j) \rangle$ is independent of k_i and k_j , the coefficients A_{ij} , $i \neq j$ are zero because of the relation

$$\left(\frac{\partial E_j}{\partial k_x^j} \right) k_j = - \left(\frac{\partial E_j}{\partial k_x^j} \right) -k_j$$

and the relaxation times are given by

$$\frac{1}{\zeta_i(E_F)} = \int_{S_i(E_F)} \left[1 - \frac{(\partial E_i / \partial k_x^i) k_i}{(\partial E_i / \partial k_x^i) k_i} P_{ii}(k_i, k'_i) dS_{k'_i} + \int_{S_j(E_F)} P_{ji}(k_i, k'_j) dS_{k'_j} \right] \quad (B.7)$$

The ratio of the d to s conductivities is given by

$$\frac{\sigma_d}{\sigma_s} = \frac{\zeta_d(E_F) N_{\text{off}}^d(E_F)}{\zeta_s(E_F) N_{\text{off}}^s(E_F)} \quad (B.8)$$

N_{off}^i being the effective number of i electrons at the Fermi level.

Expression (A.8) was estimated for the impurity problem, using free electron bands with an effective mass, one gets then :

$$\frac{\sigma_d}{\sigma_s} \approx \frac{|V_{sd}|^4 |G_s(E_F)|^2 \left(\frac{n_o^d}{n_o^s}\right)^{2/3} + \frac{m}{m^*} \left(\frac{n_{od}}{n_{os}}\right) |V_{sd}|^2}{V_{dd}^2}$$

n_o^d and n_o^s seing the n^o of holes in the d-band and the number of electron in the s-band respectively using

$$\frac{n_o^d}{n_{os}} \approx 5, \frac{m}{m^*} \approx \frac{1}{10}, |V_{sd}| \approx 0.7 \text{ eV and } V_{dd} \approx \text{eV one obtains } \frac{\sigma_d}{\sigma_s} \approx 0.2$$

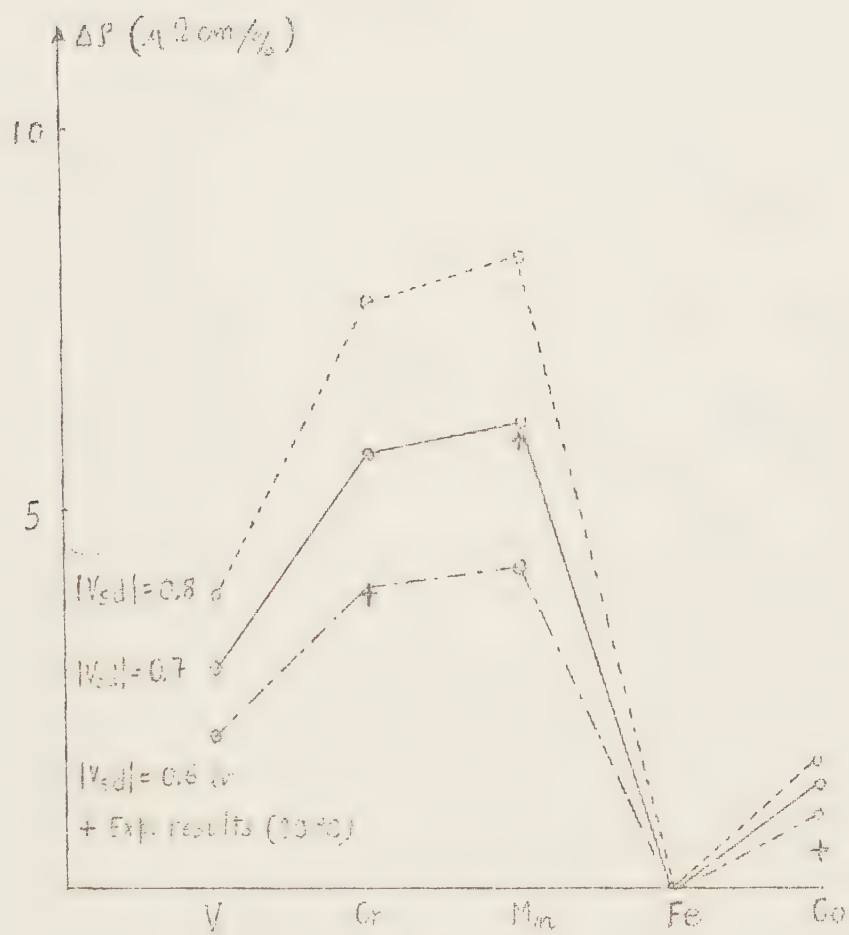


Fig. 1

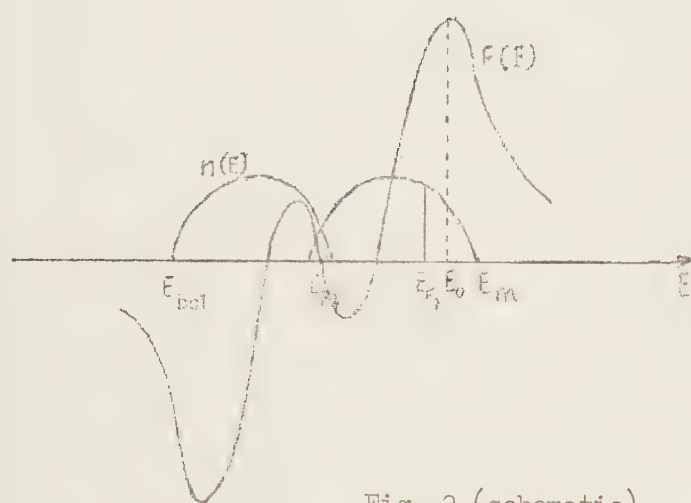


Fig. 2 (schematic)
State density and $F(E)$ curves

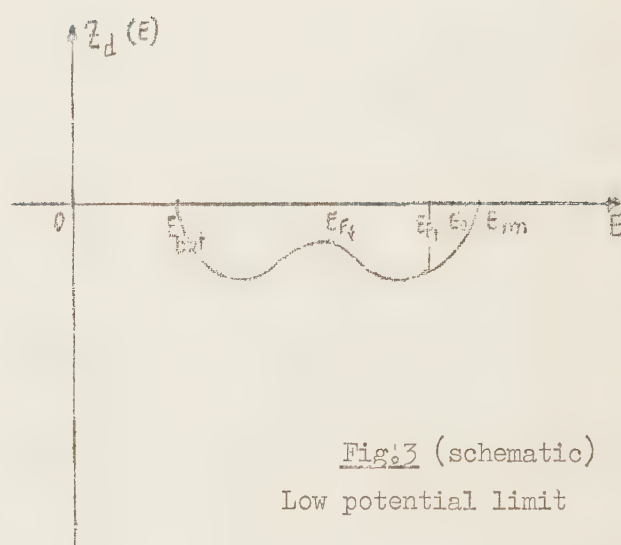


Fig. 3 (schematic)
Low potential limit

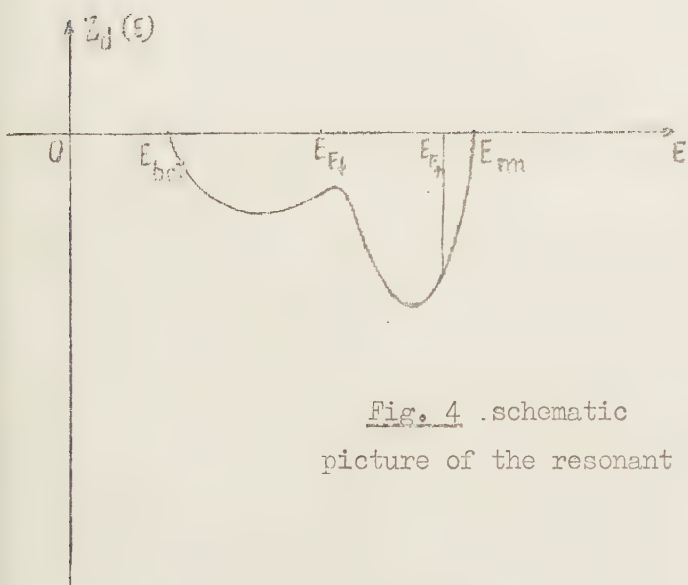


Fig. 4 .schematic
picture of the resonant case

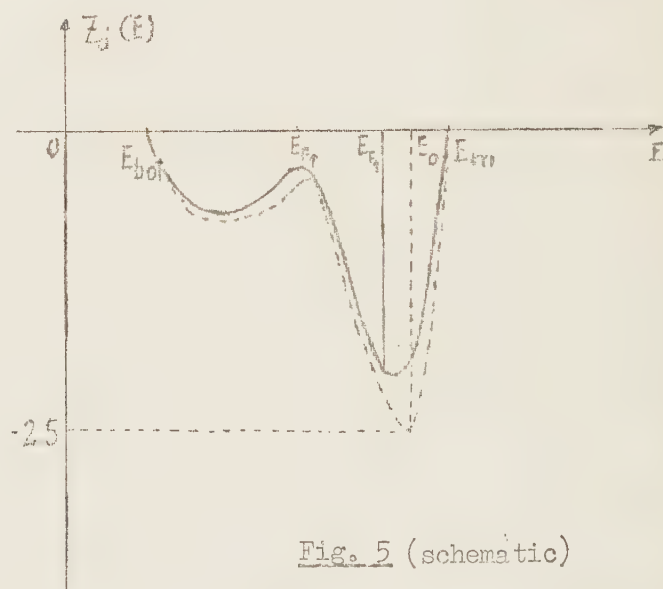


Fig. 5 (schematic)
Beginning of the anti-resonance

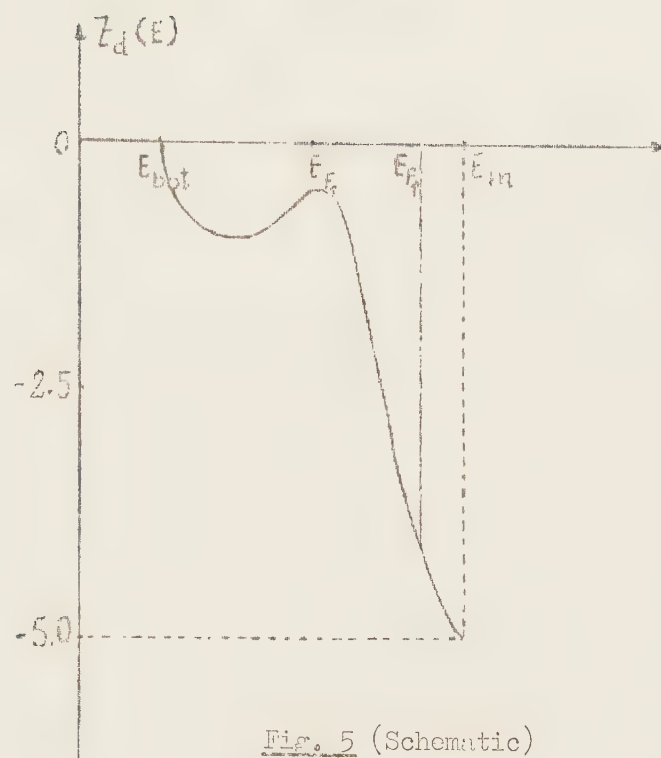


Fig. 5 (Schematic)

Anti-resonant case

Bibliography

- 1 - A. Arrott (to be published).
- 2 - A. Arrott and J.E. Noakes - Iron and its dilute alloys 1961 (Edited by C.W. Spinoe and F.E. Werner).
- 3 - N. Mott - Adv. in Phys. 1964 - Vol 13 n°51.
- 4 - J. Friedel - J. Phys. et Rad. 1962, 23, 692.
- 5 - P.A. Wolff - Phys. Rev. 1961, 124 1030.
- 6 - F. Gautier : Thesis Paris 1963.
- 7 - J. Kanamori (To be published).
- 8 - M. Asdente, J. Friedel - Phys. Rev. 1961, 124 384.
- 9 - M. Asdente (To be published)
- 10 - H.H. Wood - Phys. Rev. 1962 ; 126, 517.
- 11 - J. Yamashita, M. Fukuchi and S. Wakoh - J. Phys. Soc. of Japan 1963, 18, 999.
- 12 - F. Gautier, P. Longlart (to be published)
- 13 - A. Blandin : Thesis Paris 1961.
- 14 - A.M. Clogston, Phys. Rev. 1962, 125 439
- 15 - Mott and Jones - Theory of metals and alloys (1936), Oxford.
- 16 - Coles B.R. and Taylor J.C. 1962, Proc. Roy. Soc. A 267, 139.

CHAPITRE IV

CHALEUR SPECIFIQUE, RESISTIVITE ET POUVOIR THERMOELECTRIQUE
DES ALLIAGES DE METAUX DE TRANSITION

to be submitted to Proc. Phys. Soc.

REMARKS ON THE ELECTRONIC STRUCTURE OF TRANSITION
METAL ALLOYS

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Abstract.

The changes in electronic specific heat, residual resistivity and thermoelectric power caused by the introduction of different impurities into transition metals are calculated in the low impurity concentration limit by a localized perturbation method. The electronic structure of the pure transition metals is described by a tight binding d-band and an overlapping free electron s-band. It turns out that, in this model, simple relations connect the three quantities to the d-band structure and to the charge difference between host and impurity. The predictions of the model are shown to be frequently very different from those of the rigid band model.

I. INTRODUCTION

The experimental study of the structure of transition metal alloys is usually made through specific heat and magnetic measurements, or less directly by NMR. The theoretical basis for the interpretation of the experimental data is in the great majority of cases the rigid band model. This model suggests the technique of continuously varying the relative concentrations of the alloy components in order to "draw" the density of states curve. Recent investigations, such as those of the specific heats of dilute iron alloys {1}, show that the rigid band interpretation cannot explain consistently all the results, and often is incompatible with density of states curves calculated from band theory. Similar difficulties have been encountered in interpreting magnetic data.

There are two difficulties in this approach:

a) For non-dilute alloys the electron scattering will be modified by high concentration effects which are not well understood at the present time.

b) Even in the low concentration range, the rigid band model is valid only under restrictive conditions. These conditions depend essentially on the details of the band structure, particularly the density of states, which is precisely what the experiments are attempting to determine. It is thus difficult to know a priori if the rigid band model can be used to derive information about the band structure from the experimental data, and the results obtained should be treated with caution.

In this paper we calculate the changes in electronic specific heat, resistivity, and thermoelectric power caused by dilute impurities. Expressions for these quantities are derived which depend on simple parameters of the host band structure and on the excess impurity charge Z . From these calculations it is possible to show how these quantities behave as a function of Z for a given host band structure. The reasons for deviations from the rigid band model are discussed for some cases.

Finally, the calculations suggest a different experimental approach, which consists of measuring the specific changes for a series of dilute impurities in each host metal ; this should give information about the band structure of the host. The method is applied to some particular cases for which suitable experimental data are available (Fe, Ni) and reasonable agreement with experiment can be obtained.

II. DESCRIPTION OF THE MODEL

a) ADOPTED BAND STRUCTURE.

The transition metals are characterized by a broad conduction band (s-band) which overlaps a narrow d-band. In this simplified model we will assume that no s-d mixing is present in the pure metal, and consequently that the two bands can be treated separately. The narrow d-band will be treated within the tight binding approximation, and the s-band will be assumed to be a free electron band.

In the discussion of the electronic specific heat, the important contribution comes from the d-band because of the high value of the unperturbed d-density of states, but on the contrary, for transport phenomena the s-band carries almost all the current (Mott {2}).

Then in the case of specific heat calculations one is interested in the discussion of the scattering of the d-electrons by the impurity potential. Even in the simplified situation where the contribution of the s-electrons to the changes in density of states is neglected, one must still handle the difficulty of the d-band degeneracy. Several methods have been proposed to treat perturbations in degenerate bands {3,4,5}, and the results become particularly simple in the case of localized perturbations. In this case, the change in density of states depends only (cf. below) on the knowledge of the energy distribution of the d-orbitals of given symmetry $n_d(\epsilon, \Gamma)$.

If the d-wave functions of the pure metal are given by :

$$\psi_{\vec{k}\lambda}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_m \sum_{\lambda} A_m(\vec{k}) e^{i\vec{k} \cdot \vec{R}_\lambda} \phi_m(\vec{r} - \vec{R}_\lambda) \quad (1)$$

λ being the site position and ϕ_m being the d-atomic functions, then $n_d(\epsilon, \Gamma)$ is given by :

$$n_d(\epsilon, \Gamma) = \frac{1}{(2\pi)^3} \sum_n \int_{S_n(\epsilon)} \frac{|A_m(\vec{k}, \Gamma)|^2}{|\nabla_k \epsilon_n(k)|} dS_k \quad (2)$$

$\epsilon_n(k)$ being the dispersion relation corresponding to the n -th band.

From (2) and the normalization of the d -functions it follows that

$$n_d(\epsilon) = 3n_d(\epsilon, \Gamma'_{25}) + 2n_d(\epsilon, \Gamma'_{12}) \quad (3)$$

$n_d(\epsilon)$ being the total d -density of states of the pure metal.

In the general discussion of the changes in specific heat it will be supposed that $n_d(\epsilon, \Gamma)$ is known. Unfortunately the knowledge of this function is restricted to only a few cases,

since it requires a quite detailed band calculation. Then in comparing with experiment, we will usually assume that $n_d(\epsilon, \Gamma'_{25}) = n_d(\epsilon, \Gamma'_{12}) = n_d(\epsilon)/5$, an assumption approximately verified in the few band computations made. This is equivalent to describing the d -band by five independent sub-bands.

In the calculation of the transport properties we assume from the beginning this simplified model for the d -band structure. In fact, in this calculation one has to deal with the scattering of the s -electrons by the impurity potential. The most important processes {6} are those where the s -electrons are scattered into the d -band, or scattered to other s -states via the d -band. If the degeneracy of the d -band were to be treated properly one would have to describe the s -band by functions transforming according to the representations of the cubic group and which are orthogonal to the d -band wave functions. At the present stage no simple method of doing this is available ; thus we adopt this crude picture to describe the impurity induced s - d scattering processes.

Finally the band structure of ferromagnetic metals will be described by the Stoner model, where the polarization of the s -band is neglected.

b) DESCRIPTION OF THE IMPURITY POTENTIAL.

In this paper the phenomenological description of the impurity potential will be adopted.

One starts assuming the potential to be localized within the impurity cell, and then determines it by imposing Friedel's screening condition. Actually one should solve the complete scattering problem (s and d bands) and impose that the total number of states introduced by the perturbation is equal to the excess charge of the impurity. An approximate calculation (6) shows that the screening produced within the s-band by ss scattering and by the impurity induced s-d mixing is small compared to the screening produced by the d-electrons because $n_s(\epsilon_F) \ll n_d(\epsilon_F)$.

Then it will be assumed in this paper that the excess charge Z introduced by the impurities is completely screened within the d-band. From this assumption it is possible to determine the d-d matrix elements from the value of Z. We divide this discussion into two parts :

1) Paramagnetic metals.

We adopt the Hartree picture for the localized impurity potential, and assume that the point symmetry is not destroyed by the introduction of the impurity.

Then only the following matrix elements appear in the scattering problem {4} :

$$\langle \phi_{d\Gamma}(\vec{r}) | V(\vec{r}) | \phi_{d\Gamma}(\vec{r}) \rangle \quad (4) \quad (\Gamma = \Gamma'_{25}, \Gamma_{12})$$

$\phi_d(\vec{r})$ being atomic functions of Γ symmetry centred at the origin.

If one supposes further that $V(\vec{r})$ has quasi-spherical symmetry, one is reduced to

$$V_{dd} = \langle \phi_{d\Gamma'_{25}} | V | \phi_{d\Gamma'_{25}} \rangle = \langle \phi_{d\Gamma_{12}} | V | \phi_{d\Gamma_{12}} \rangle \quad (5)$$

The value of V_{dd} is determined by Friedel's screening condition which is in this case {4} :

$$Z = \frac{2}{\pi} \sum_{\Gamma} n_{\Gamma} \delta_d(\epsilon_F, \Gamma) \quad (6)$$

The phase shift $\delta(\epsilon, \Gamma)$ being defined by

$$\delta_d(\epsilon, \Gamma) = - \arctg \frac{\pi V_{dd} n_d(\epsilon, \Gamma)}{1 - V_{dd} F_d(\epsilon, \Gamma)} \quad (7)$$

In expressions (6) and (7) n_{Γ} is the multiplicity of the Γ representation ($n_{\Gamma_{12}} = 2$ and $n_{\Gamma_{25}} = 3$) and $F_d(\epsilon, \Gamma)$ is the Hilbert transform of $n_d(\epsilon, \Gamma)$.

Then for the paramagnetic metals, expressions (6) and (7) solve the problem of the self-consistent determination of V_{dd} as a function of Z and of the band structure.

2) Ferromagnetic metals.

In this case, due to exchange the two spin sub-bands of the pure metal are split off. There are two important differences with respect to the paramagnetic case. Firstly, in the expressions (6) and (7) one should separate the two spin directions and introduce the functions $F_{d\sigma}(\epsilon, \Gamma)$ and $n_{\sigma}(\epsilon, \Gamma)$ (σ denoting the spin), which are determined in the Stoner picture only by the splitting of the two sub-bands. Secondly the Hartree picture is not suitable to describe the impurity potential in ferromagnetic alloys, and should be replaced by the Hartree-Fock picture.

An evidence of this failure is provided by the magnetic moment of transition impurities dissolved in iron {7}.

The Hartree picture is improved {7} by describing the impurity by two potentials $V_{dd}^{\uparrow}$ and $V_{dd}^{\downarrow}$ which should satisfy simultaneously the Hartree-Fock equation and Friedel's screening condition which is in this case :

$$Z = \frac{1}{\pi} \sum_{\sigma} \sum_{\Gamma} n_{\Gamma} \delta_{\sigma}(\epsilon_F, \Gamma) \quad (8)$$

The phase shift $\delta_\sigma(\epsilon, \Gamma)$ being defined by :

$$\delta_\sigma(\epsilon, \Gamma) = - \operatorname{arctg} \frac{\pi V_{dd}^\sigma n_{d\sigma}(\epsilon, \Gamma)}{1 - V_{dd}^\sigma F_{d\sigma}(\epsilon, \Gamma)} \quad (9)$$

As discussed in {7} the Hartree-Fock equation becomes rather cumbersome to solve in presence of the degeneracy of the d-band because it requires the detailed knowledge of the exchange integral between the several d-orbitals.

There are two possible choices at this stage, in order to obtain V_{dd}^σ . The first one is to adopt the approximation of five equivalent sub-bands and solve the Hartree-Fock equation and (8) simultaneously as is done in {7}. The second is to use the measured data of the change in averaged magnetic moment $\frac{d\bar{\mu}}{dc}$ to compute the displaced charge in the $\uparrow$ and $\downarrow$ sub-bands.

In fact one has, combining the screening condition $Z = Z_\uparrow + Z_\downarrow$ and the equation $\frac{d\bar{\mu}}{dc} = Z_\uparrow - Z_\downarrow$:

$$\begin{aligned} Z_\uparrow &= \frac{1}{2} \left(Z + \frac{d\bar{\mu}}{dc} \right) \\ Z_\downarrow &= \frac{1}{2} \left(Z - \frac{d\bar{\mu}}{dc} \right) \end{aligned} \quad (10)$$

From (10) and (9) it is possible to compute the values of $V_{dd}^\uparrow$ and $V_{dd}^\downarrow$ as a function of Z , $\frac{d\bar{\mu}}{dc}$ and $n_\sigma(\epsilon, \Gamma)$.

In the case of iron alloys the last procedure is equivalent to solving the Hartree-Fock equation because the observed change in sign of $\frac{d\bar{\mu}}{dc}$ is an effect which is impossible to describe within the Hartree picture.

In the case of transport properties the matrix element $V_{sd} = \langle \phi_s(k, \vec{\Gamma}) | V(\vec{\Gamma}) | \phi_d(k', \Gamma) \rangle$ plays the essential role of inducing the s-d transitions responsible for the changes in these properties. One will adopt in this paper the crude approximation of the independence of V_{sd} on k and k' , as was done before {6}.

III. GENERAL RESULTS.

In this paragraph we discuss the general formula relating the changes in electronic specific heat, resistivity and thermoelectric power to the band structure in the low impurity concentration limit. For each of these quantities we separate the cases of paramagnetic and ferromagnetic alloys.

1) ELECTRONIC SPECIFIC HEAT.

a) Paramagnetic metals.

The change in electronic specific heat per unit impurity concentration is related to the phase shift (7) by the relation :

$$\frac{\Delta\gamma}{\Delta c}(c=0) = \alpha \frac{1}{\pi} \sum_{\Gamma} n_{\Gamma} \left\{ \frac{\partial}{\partial \epsilon} \delta_d(\epsilon, \Gamma) \right\}_{\epsilon_F} \quad (11)$$

where $\alpha = \frac{2}{3} \pi^2 k_{\beta}^2$

The expression (11) together with (6) and (7) gives the change in specific heat as a function of Z and the band structure.

In principle it is possible to find an analytical expression for V_{dd} which satisfies (7) for a given Z and substitute it in (11) getting $\frac{\Delta\gamma}{\Delta c}$ directly as a function of Z, $F_d(\epsilon_F, \Gamma)$ and $n_d(\epsilon_F, \Gamma)$. Actually the expression for $\frac{\Delta\gamma}{\Delta c}$ obtained in this way is rather cumbersome to work out in the general case. It becomes however extremely simple in the approximation $n_d(\epsilon, \Gamma) = n_d(\epsilon)/5$ and enables a very simple qualitative discussion of the changes in specific heat with Z.

In this approximation, equations (7) and (11) become :

$$Z = - \frac{10}{\pi} \operatorname{arctg} \frac{\pi V_{dd} n_d(\epsilon_F)/5}{1 - V_{dd} F_d(\epsilon_F)/5} \quad (12)$$

$$\frac{\Delta Y}{\Delta c}(c=0) = \frac{5\alpha}{\pi} \frac{\partial}{\partial \epsilon} \left\{ - \operatorname{arctg} \frac{\pi V_{dd} n_d(\epsilon)/5}{1 - V_{dd} F_d(\epsilon)/5} \right\}_{\epsilon_F} \quad (13)$$

Combining (12) and (13) one finally obtains :

$$\frac{\Delta Y}{\Delta c}(c=0) = \frac{5\alpha \sin \frac{\pi Z}{5}}{2\pi n(\epsilon_F)} \left\{ \frac{n}{d\epsilon}(\epsilon_F) - \frac{1}{\pi} \frac{F}{d\epsilon}(\epsilon_F) \operatorname{tg} \frac{\pi Z}{10} \right\} \quad (14)$$

From (14) one sees that, apart the multiplicative factor $\frac{5}{2\pi n(\epsilon_F)} \frac{n}{d\epsilon}(\epsilon_F)$ the changes in specific heat as a function of Z are determined only by the ratio :

$$R(\epsilon_F) = \frac{dF}{d\epsilon}(\epsilon_F) / \frac{dn}{d\epsilon}(\epsilon_F) \quad (15)$$

A more detailed discussion of (14) will be given later.

b) Ferromagnetic metals.

In this case the expression (11) should be replaced by :

$$\frac{\Delta Y}{\Delta c}(c=0) = \frac{\alpha}{2\pi} \sum_{\sigma} \sum_{\Gamma} n_{\Gamma} \left\{ \frac{\partial}{\partial \epsilon} \delta_{d\sigma}(\epsilon, \Gamma) \right\} \quad (16)$$

Within the spirit of (10), and for the general case of $n_d(\epsilon, \Gamma)$, there is no simple formula relating $\frac{\Delta Y}{\Delta c}(c=0)$, Z and $\frac{dF}{dc}$. One should compute numerically the values of $V_{dd}^{\uparrow}$ and $V_{dd}^{\downarrow}$ from $Z_{\sigma} = \frac{1}{\pi} \sum_{\Gamma} n_{\Gamma} \delta_{\sigma}(\epsilon_F, \Gamma)$ and substitute then in (16).

Within the approximation of five independent sub-bands, things become considerably simpler. In fact, equations (12) and (13) should now be replaced by :

$$Z_{\sigma} = - \frac{5}{\pi} \operatorname{arctg} \frac{\pi V_{dd}^{\sigma} n_{d\sigma}(\epsilon_F)/5}{1 - V_{dd}^{\sigma} F_{d\sigma}(\epsilon_F)/5} \quad (17a)$$

and

$$\frac{\Delta\gamma_{\sigma}}{\Delta c}(c=0) = \frac{5\alpha}{2\pi} \frac{\partial}{\partial \epsilon} \left\{ - \operatorname{arctg} \frac{\pi V_{dd}^{\sigma} n_d^{\sigma}(\epsilon_F)/5}{1 - V_{dd}^{\sigma} F_{d\sigma}(\epsilon_F)/5} \right\} \quad (17b)$$

Combining these equations one obtains for the change in specific heat :

$$\frac{\Delta\gamma}{\Delta c}(c=0) = \frac{5\alpha}{4\pi} \sum_{\sigma} \sin \frac{2\pi Z_{\sigma}}{5} \left\{ \frac{dn_{\sigma}}{d\epsilon}(\epsilon_F) - \frac{1}{\pi} \frac{dF_{\sigma}}{d\epsilon}(\epsilon_F) \operatorname{tg} \frac{\pi Z_{\sigma}}{5} \right\} \quad (18)$$

where Z_{σ} is determined by (10), and $\frac{d\bar{\mu}}{dc}$ may now be calculated as a function of the band structure using the methods of {7}.

Expression (18) shows that the contribution of each spin sub-band is now easily discussed as a function of $R_{\sigma}(\epsilon_F) = \frac{dF_{\sigma}}{d\epsilon}(\epsilon_F) / \frac{dn_{\sigma}}{d\epsilon}(\epsilon_F)$, Z and $\frac{d\bar{\mu}}{dc}$.

2) CHANGES IN ELECTRICAL RESISTIVITY.

a) Paramagnetic metals.

a-1) General results.

Within the approximations described in paragraphs I-a) and I-b) the residual resistivity due to a low impurity concentration is given by {6} :

$$\Delta\rho = \beta \frac{5 |V_{sd}|^4 |G_d(\epsilon_F)/5|^2 n_s(\epsilon_F) + |V_{sd}|^2 n_d(\epsilon_F)}{[1 - V_{dd} F_d(\epsilon_F)/5]^2 + [\pi V_{dd} n_d(\epsilon_F)/5]^2} \quad (19)$$

where $\beta = \frac{4\pi mc}{e^2 \hbar N_a}$, N_a being the number of atoms p / unit volume and c the concentration.

The first term of (19) corresponds to the process where one electron in a s -state is scattered into another s -state via

the d-band, and the second describes the scattering from a s-state to a d-state. The term is a pure d-band effect and only occurs because of the finite width of the d-band.

Expression (19) can be rewritten in a quite illuminating way if one introduces the phase shift $\delta(\epsilon, V_{dd})$ as defined by (12).

In fact it follows from (12) that

$$\frac{\partial \delta(\epsilon, V_{dd})}{\partial V_{dd}} = - \frac{\pi n_d(\epsilon)/5}{[1 - V_{dd} F_d(\epsilon)/5]^2 + [\pi V_{dd} n_d(\epsilon)/5]^2} \quad (20)$$

and then (19) becomes :

$$\Delta \rho = - \frac{5\beta}{\pi} \left\{ |V_{sd}|^4 \frac{|G_d(\epsilon_F)|^2}{5 n_d(\epsilon_F)} n_s(\epsilon_F) + |V_{sd}|^2 \right\} \frac{\partial \delta_d(\epsilon_F, V_{dd})}{\partial V_{dd}} \quad (21)$$

The residual resistivity is then simply related to the derivative of the d-phase shift at the Fermi level. Consequently the occurrence of bound states, resonant states etc, affect the resistivity in a way that is rather simple to discuss.

In order to get the residual resistivity as an explicit function of Z we combine (12) and (20) to get :

$$\begin{aligned} \frac{\partial \delta(\epsilon_F, V_{dd})}{\partial V_{dd}} &= - \frac{\cos^2 \frac{\pi Z}{10}}{5 \pi^2 n_d(\epsilon_F)} F_d^2(\epsilon_F) \left\{ \frac{\pi n_d(\epsilon_F)}{F_d(\epsilon_F)} - \operatorname{tg} \frac{\pi Z}{10} \right\}^2 \\ &= \frac{1}{5 \pi^2 n_d(\epsilon_F)} \left\{ \pi n_d(\epsilon_F) \cos \frac{\pi Z}{10} - F_d(\epsilon_F) \sin \frac{\pi Z}{10} \right\}^2 \end{aligned} \quad (22)$$

We can introduce the phase θ_R defined by the relations :

$$\cos \theta_R = \frac{\pi n_d(\epsilon_F)}{\sqrt{F_d^2(\epsilon_F) + \pi^2 n_d^2(\epsilon_F)}} \quad (23)$$

$$\sin \theta_R = \frac{F_d(\epsilon_F)}{\sqrt{F_d^2(\epsilon_F) + \pi^2 n_d^2(\epsilon_F)}}$$

Using this definition (22) can be rewritten :

$$\frac{\partial \delta(\epsilon, V_{dd})}{\partial V_{dd}} = - \frac{F_d^2(\epsilon_F) + \pi^2 n_d^2(\epsilon_F)}{5\pi^2 n_d(\epsilon_F)} \cos^2\left(\frac{\pi Z}{10} + \theta_R\right) \quad (24)$$

From (24) one sees that the following relation is valid :

$$\left| \frac{\partial \delta}{\partial V_{dd}}(Z \pm 5) \right| + \left| \frac{\partial \delta}{\partial V_{dd}}(Z) \right| = \left| \frac{\partial \delta}{\partial V_{dd}}(\pm 5) \right| + \left| \frac{\partial \delta}{\partial V_{dd}}(0) \right| \quad (25)$$

The expression for the resistivity is then :

$$\Delta \rho = \beta \left\{ |V_{sd}|^4 \frac{|G_d(\epsilon_F)|^2}{5n_d(\epsilon_F)} n_s(\epsilon_F) + |V_{sd}|^2 \right\} \frac{|G_d(\epsilon_F)|^2}{\pi^3 n_d(\epsilon_F)} \cos^2\left(\frac{\pi Z}{10} + \theta_R\right) \quad (26)$$

a-2) Estimate of the $|V_{sd}|$ matrix element.

We stress that equation (26) is only valid if the screening of the impurity excess charge is entirely performed within the d-band. Let us define the strength V_0 of the potential by $V(\vec{r}) = V_0 v(\vec{r})$, $v(\vec{r})$ giving the shape of the potential, V_0 is completely determined by equation (12) provided that the shape $v(\vec{r})$ does not change with Z .

The last assumption is certainly an over simplification of the problem but it provides an estimate of the variation of $|V_{sd}|$ as a function of Z .

Let's introduce the parameter α_{sd} as defined by :

$$\alpha_{sd} = \frac{\int \varphi_s^*(\vec{r}) v(\vec{r}) \varphi_d(\vec{r}) d}{\int \varphi_d^*(\vec{r}) v(\vec{r}) \varphi_d(\vec{r}) d} \quad (27)$$

One may have a rough estimate of (27) taking for φ_s and φ_d plane waves and d-functions respectively, and some kind of reasonable potential such that $\frac{1}{\Omega} \int v(\vec{r}) d\vec{r} = 1$. Any way α_{sd} can be considered as the parameter of the model, but it is usually a small quantity, as compared to one.

From these considerations it follows that $|V_{sd}|^2 = |\alpha_{sd}|^2 V_{dd}^2$ which combined with (12) gives for $|V_{sd}|^2$:

$$|V_{sd}|^2 = \frac{25 |\alpha_{sd}|^2 \operatorname{tg}^2 \frac{\pi Z}{10}}{\left[\pi n_d(\epsilon_F) - F_d(\epsilon_F) \operatorname{tg} \frac{\pi Z}{10} \right]^2} \quad (28)$$

One sees from (28) that $|V_{sd}|^2 = 0$ for $Z = 0$ as expected, and for $Z = \pm 5$, $|V_{sd}|^2 = \frac{25 |\alpha_{sd}|^2}{F_d^2(\epsilon_F)}$.

It is to be noted also that for $Z \rightarrow Z_m$ (maximum displaced charge, $|V_{sd}|^2 \rightarrow +\infty$ as expected from the fact that the potential strength becomes infinitely repulsive or attractive. It follows from (28) that for $\frac{\pi n_d(\epsilon_F)}{F_d(\epsilon_F)} \ll 1$, which corresponds to a high value of Z_m , the derivative $\frac{d|V_{sd}|}{dZ}$ is rather small except for Z values close to zero, or close to Z_m . Then for the cases of physical interest (Z integral) $|V_{sd}|^2$ is almost constant.

We can also estimate the order of magnitude of the term $a(Z) = |V_{sd}|^4 \frac{|G_d(\epsilon_F)|^2}{5 n_d(\epsilon_F)} n_s$ as compared to $|V_{sd}|^2$. This is done assuming the relations : (usually satisfied for ϵ_F near the top of the band) $F_d(\epsilon_F) \approx 3 n_d(\epsilon_F)$ and $n_s/n_d \approx 0.1$. From (28) one gets :

$$\frac{a(Z)}{|V_{sd}|^2} \approx \frac{|\alpha_{sd}|^2}{\left[1 - \frac{\pi n_d(\epsilon_F)}{F_d(\epsilon_F)} \cotg \frac{\pi Z}{10}\right]^2} \quad (29)$$

This expression shows that $a(Z)$ is smaller than $|V_{sd}|^2$ by a factor $|\alpha_{sd}|^2$ at $Z = \pm 5$ and increasingly smaller for $|Z|$ decreasing to zero.

This estimates suggest that the $|V_{sd}|^2$ matrix element may be considered as slowly varying as a function of Z in a rather wide region, and that the second term of the resistivity (scattering of s-electrons into the d-band) is the dominant one for usual paramagnetic metals.

a-3) Final results.

Expression (26) can be highly simplified if we use the results for the V_{sd} matrix elements discussed in a-2).

In fact, equation (28) can be rewritten as :

$$|V_{sd}|^2 = \frac{25 |\alpha_{sd}|^2 \sin^2 \frac{\pi Z}{10}}{\left[\pi n_d(\epsilon_F) \cos \frac{\pi Z}{10} - F_d(\epsilon_F) \sin \frac{\pi Z}{10}\right]^2} \quad (30)$$

If one combines equations (21), (22) and (30) it follows that the resistivity can be written as :

$$\Delta\rho = \frac{25\beta |\alpha_{sd}|^2}{\pi^3 n_d(\epsilon_F)} \sin^2 \frac{\pi Z}{10} \left\{ 1 + \frac{n_s(\epsilon_F)}{n_d(\epsilon_F)} |G_d(\epsilon_F)|^2 |\alpha_{sd}|^2 |V_{sd}|^2 \right\} \quad (31)$$

From (31) it can be deduced that :

i) Because of the discussion of a-2) the second term is slowly varying with Z and then the resistivity varies like a sine squared.

ii) The important mechanism for the resistivity is the scattering of s-electrons into the d-band.

iii) The changes in resistivity should be connected by the following relation :

$$\Delta\rho(Z \pm 5) + \Delta\rho(Z) = \text{constant}.$$

The remarks i) and iii) provide a simple experimental test for the validity of the approximations used in the resistivity calculation.

b) Ferromagnetic metals.

This is a particularly difficult case to discuss because apart from the complications introduced by the exchange effects (Cf. IIb) there are the extra complications introduced by the deviations from Mathiessen rule {8}.

The simplest case to discuss is the high temperature limit. Here the mean free path of the carriers before collisions with impurities is large compared to that associated with collisions with spin waves.

From this fact one has for the change in resistivity due to the impurities {6}

$$\Delta\rho = \frac{1}{2} (\Delta\rho_{\uparrow} + \Delta\rho_{\downarrow}) \quad (32)$$

when $\Delta\rho_{\sigma}$ is the change in resistivity of the σ -spin s-electrons.

From (19) one has :

$$\Delta\rho_{\sigma} = \frac{\beta}{2} \frac{5 |V_{sd}^{\sigma}|^4 |G_{d\sigma}(\epsilon_F)/5|^2 n_s(\epsilon_F) + |V_{sd}^{\sigma}|^2 n_{d\sigma}(\epsilon_F)}{[1 - V_{dd}^{\sigma} F_{d\sigma}(\epsilon_F)/5]^2 + [\pi V_{dd}^{\sigma} n_{d\sigma}(\epsilon_F)/5]^2} \quad (33)$$

We may now reproduce the reasoning of paragraph III2 to transform (32) using (17a). One obtains for $\Delta\rho_{\sigma}$:

$$\Delta\rho_{\sigma} = \frac{\beta}{2} \left\{ |v_{sd}^{\sigma}|^4 \frac{G_d^{\sigma}(\epsilon_F)^2}{5n_{d\sigma}(\epsilon_F)} n_s(\epsilon_F) + |v_{sd}^{\sigma}|^2 \right\} \\ \frac{|G_d(\epsilon_F)|^2}{\pi^3 n_{d\sigma}(\epsilon_F)} \cos^2\left(\frac{\pi Z_{\sigma}}{5} + \theta_{R\sigma}\right) \quad (34)$$

where the phase angle is defined by $\operatorname{tg} \theta_{R\sigma} = \frac{F_{d\sigma}(\epsilon_F)}{\pi n_{d\sigma}(\epsilon_F)}$

The mixing matrix elements $|v_{sd}^{\sigma}|$ are now connected to the band structure and Z by :

$$|v_{sd}^{\sigma}|^2 = \frac{25 |\alpha_{sd}|^2 \operatorname{tg}^2 \frac{\pi Z_{\sigma}}{5}}{\left[\pi n_{d\sigma}(\epsilon_F) - F_{d\sigma}(\epsilon_F) \operatorname{tg} \frac{\pi Z_{\sigma}}{5} \right]^2} \quad (35)$$

if one assumes that the Hartree-Fock effects are present in $V(\vec{r})$ only through the strength V_0^{σ} of the potential.

Again the use of (35) simplifies the expression (34) for the resistivity and one gets :

$$\Delta\rho = \frac{25 \beta |\alpha_{sd}|^2}{\pi^3} \sum_{\sigma} \frac{1}{n_{d\sigma}} \sin^2 \frac{\pi Z_{\sigma}}{5} \left\{ 1 + \frac{n_s(\epsilon_F)}{n_{d\sigma}(\epsilon_F)} |G_{d\sigma}(\epsilon_F)|^2 |\alpha_{sd}| |v_{sd}^{\sigma}|^2 \right\} \quad (36)$$

3) CHANGES IN THERMO-ELECTRIC POWER.

a) Paramagnetic metals.

a-1) General expression.

According to Friedel {9} the change in thermo-electric power can be rigourously written :

$$\frac{\Delta S}{S} = - \frac{1 - \frac{\Delta x}{x}}{1 + \frac{\rho}{\Delta \rho}} \quad (37)$$

S being the absolute thermo-electric power and ρ the resistivity of the pure metal ; and x, Δx are defined as :

$$x = \left[\frac{\partial}{\partial \epsilon} \log \rho \right]_{\epsilon_F} \quad (38)$$

$$\Delta x = \left[\frac{\partial}{\partial \epsilon} \log \Delta \rho \right]_{\epsilon_F}$$

We calculate Δx from (19) assuming that $\frac{d}{d\epsilon} n_s(\epsilon_F) \approx 0$. This approximation seems quite reasonable since the s-band is a rather broad and flat band.

From (19) one gets then :

$$\Delta x = \left[\frac{\partial}{\partial \epsilon} \log \left| \frac{\partial \delta(\epsilon, V_{dd})}{\partial V_{dd}} \right| \right]_{\epsilon_F} \quad (37)$$

$$+ \frac{|V_{sd}|^4 n_s(\epsilon_F) \left\{ \frac{\partial}{\partial \epsilon} \frac{|G_d(\epsilon)|^2}{5 n_d(\epsilon)} \right\} + \frac{|G_d(\epsilon_F)|^2}{5 n_d(\epsilon_F)} n_s \frac{\partial}{\partial \epsilon} |V_{sd}|^4_{\epsilon_F} + \frac{\partial}{\partial \epsilon} |V_{sd}|^2_{\epsilon_F}}{|V_{sd}|^4 \frac{|G_d(\epsilon_F)|^2}{5 n_d(\epsilon_F)} n_s(\epsilon_F) + |V_{sd}|^2}$$

Expression (37) shows that the change in thermo-electric power appears to come from the sum of two contributions :

- i) The change in d-d scattering with energy.
- ii) The change with energy of the quantities describing the s-d mixing effect.

a-2) Evaluation of the derivatives of the V_{sd} matrix elements.

Equation (28) provides a relation between $|V_{sd}|^2$, Z and the band structure.

From this relation it should be possible to calculate $\frac{\partial}{\partial \epsilon} |V_{sd}|^2$ as a function of these parameters. The only parameter for which the energy dependence is not known is $|\alpha_{sd}|$ (cf. (27)).

We assume in this calculation that $|\alpha_{sd}|$ varies slowly with ϵ , which seems to be reasonable for localized potentials.

Within this approximation ($\frac{\partial}{\partial \epsilon} |\alpha_{sd}|^2 \approx 0$) it follows from (28) that :

$$\begin{aligned} \frac{\partial}{\partial \epsilon} |V_{sd}|^2_{\epsilon_F} &\approx -2 |V_{sd}|^2 f(Z) \\ f(Z) &= \frac{\frac{dF_d}{d\epsilon}(\epsilon_F) \operatorname{tg} \frac{\pi Z}{10} - \pi \frac{dn_d}{d\epsilon} + \frac{\pi^2 n_d(\epsilon_F)}{5 \sin^2 \pi Z/6} \frac{dZ}{d\epsilon}(\epsilon_F)}{F_d(\epsilon_F) \operatorname{tg} \frac{\pi Z}{10} - \pi n_d(\epsilon_F)} \end{aligned} \quad (38)$$

Now we want to show that $f(Z)$ is exactly zero.

In fact, from (14) one has :

$$\frac{\pi^2 n_d(\epsilon_F)}{5 \sin \frac{\pi Z}{5}} \frac{dZ}{d\epsilon}(\epsilon_F) = \pi \frac{dn_d}{d\epsilon} - \frac{dF_d}{d\epsilon}(\epsilon_F) \operatorname{tg} \frac{\pi Z}{10} \quad (39)$$

which shows that $f(Z)$ is zero.

Then one gets from (37) the following expression for Δx :

$$\Delta x = \left[\frac{\partial}{\partial \epsilon} \log \left| \frac{\partial \delta(\epsilon, V_{dd})}{\partial V_{dd}} \right| \right]_{\epsilon_F} + \frac{|V_{sd}|^4 n_s(\epsilon_F) \left\{ \frac{\partial}{\partial \epsilon} \frac{|G_d(\epsilon_F)|^2}{5 n_d(\epsilon_F)} \right\}_{\epsilon_F}}{|V_{sd}|^4 \frac{|G_d(\epsilon_F)|^2}{5 n_d(\epsilon_F)} n_s(\epsilon_F) + |V_{sd}|^2} \quad (40)$$

a-3) General remarks about (40).

In the second term of (40), the factor $\left\{ \frac{\partial}{\partial \epsilon} \frac{|G_d(\epsilon_F)|^2}{5n_d(\epsilon_F)} \right\}_{\epsilon_F}$ depends only on the ratio $\frac{F_d(\epsilon_F)}{n_d(\epsilon_F)}$ and on the derivatives $\frac{dn_d}{d\epsilon}(\epsilon_F)$ and $\frac{dF_d}{d\epsilon}(\epsilon_F)$ in the following way :

$$\left\{ \frac{\partial}{\partial \epsilon} \frac{|G_d(\epsilon_F)|^2}{5n_d(\epsilon_F)} \right\}_{\epsilon_F} = - \frac{2}{5} \frac{F_d(\epsilon_F)}{n_d(\epsilon_F)} \frac{dF_d}{d\epsilon}(\epsilon_F) - \frac{1}{5} \frac{dn_d}{d\epsilon}(\epsilon_F) \left[\left(\frac{F_d(\epsilon_F)}{n_d(\epsilon_F)} \right)^2 - \pi^2 \right] \quad (41)$$

From the previous discussion of the resistivity (Cf.III2) it follows that the second term of (40) varies slowly with Z, and can be written approximatively as :

$$|V_{sd}|^2 n_s(\epsilon_F) \left\{ \frac{\partial}{\partial \epsilon} \frac{|G_d(\epsilon_F)|^2}{5n_d(\epsilon_F)} \right\}_{\epsilon_F} \quad (42)$$

The last conclusion follows from the fact that

$$|V_{sd}|^2 \gg |V_{sd}|^4 \frac{|G_d(\epsilon_F)|^2}{5n_d(\epsilon_F)} n_s(\epsilon_F) \text{ for usual paramagnetic metals.}$$

The first term of (40) can be rewritten as a function of Z in a way similar to the previous cases.

One calculate $\frac{\partial}{\partial \epsilon} \log \left| \frac{\partial \delta(\epsilon, V_{dd})}{\partial V_{dd}} \right|$ as a function of V_{dd} and then uses equation (12) to eliminate the potential getting :

$$\frac{\partial}{\partial \epsilon} \left\{ \log \left| \frac{\partial \delta(\epsilon, V_{dd})}{\partial V_{dd}} \right| \right\} = \frac{1}{n_d(\epsilon_F)} \left\{ \frac{dn_d}{d\epsilon}(\epsilon_F) \cos \frac{\pi Z}{5} - \frac{1}{\pi} \frac{dF_d}{d\epsilon}(\epsilon_F) \sin \frac{\pi Z}{5} \right\} \quad (43)$$

Again one introduces the phase angle θ_p defined by :

$$\sin \theta_p = \frac{\frac{dn_d}{d\epsilon}(\epsilon_F)}{\sqrt{\frac{1}{\pi^2} \left(\frac{dF_d}{d\epsilon} \right)^2 + \left(\frac{dn_d}{d\epsilon} \right)^2}} \quad (44)$$

$$\cos \theta_p = \frac{\frac{1}{\pi} \frac{dF}{d\epsilon}(\epsilon_F)}{\sqrt{\frac{1}{\pi^2} \left(\frac{dF}{d\epsilon}\right)^2 + \left(\frac{d_{nd}}{d\epsilon}\right)^2}} \quad (44)$$

to get finally :

$$\frac{\partial}{\partial \epsilon} \left\{ \log \left| \frac{\partial \delta(\epsilon, V_{dd})}{\partial V_{dd}} \right| \right\}_{\epsilon_F} = - \sqrt{\frac{1}{n_d^2(\epsilon_F)} \left[\frac{1}{\pi^2} \left(\frac{dF}{d\epsilon}\right)^2 + \left(\frac{d_{nd}}{d\epsilon}\right)^2 \right]} \sin\left(\frac{\pi Z}{5} - \theta_p\right) \quad (45)$$

Then apart from the multiplicative factor, the variation of the thermo-electric power is completely determined by the ratio $R(\epsilon_F) = \frac{dF/d\epsilon}{d_{nd}/d\epsilon}$ which is the same parameter as for the changes in specific heat.

b) Ferromagnetic metals.

These metals, even in the simplest case of high temperatures, there is no simple formula for the change Δx . In fact Δx should be in this case :

$$\Delta x = \frac{\Delta \rho_{\uparrow}}{2\Delta \rho} \Delta x_{\uparrow} + \frac{\Delta \rho_{\downarrow}}{2\Delta \rho} \Delta x_{\downarrow} \quad (46)$$

$$\text{where } \Delta x_{\sigma} = \left[\frac{\partial}{\partial \epsilon} \log \Delta \rho_{\sigma} \right]_{\epsilon_F} .$$

In (46) one sees that the contribution Δx_{σ} of the σ -electrons to x is weighted by their contribution to the total change in resistivity.

As in the case of paramagnetic metals the quantity Δx_{σ} is made of two contributions :

$$\Delta x_{\sigma} = \left[\frac{\partial}{\partial \epsilon} \log \left| \frac{\partial \delta_{\sigma}(\epsilon, V_{dd}^{\sigma})}{\partial V_{dd}^{\sigma}} \right| \right]_{\epsilon_F} \quad (47)$$

$$+ \frac{|V_{sd}|^4 n_s(\epsilon_F) \frac{\partial}{\partial \epsilon} \left\{ \frac{|G_{d\sigma}(\epsilon)|}{5 n_{d\sigma}(\epsilon)} \right\} + \frac{|G_{d\sigma}(\epsilon_F)|^2}{5 n_{d\sigma}(\epsilon_F)} n_s \frac{\partial}{\partial \epsilon} |V_{sd}|^4_{\epsilon_F} + \frac{\partial}{\partial \epsilon} |V_{sd}|^2_{\epsilon_F}}{|V_{sd}|^4 \frac{|G_{d\sigma}(\epsilon_F)|^2}{5 n_{d\sigma}(\epsilon_F)} n_s(\epsilon_F) + |V_{sd}|^2}$$

Again we can use expression (35) and (18) to show that

$\frac{\partial}{\partial \epsilon} |V_{sd}|^2_{\epsilon_F} = 0$, following the same type of argument as in the case of paramagnetic metals.

The expression for Δx_{σ} becomes then

$$\Delta x_{\sigma} = \left[\frac{\partial}{\partial \epsilon} \log \left| \frac{\partial \delta_{\sigma}(\epsilon, V_{dd}^{\sigma})}{\partial V_{dd}^{\sigma}} \right| \right]_{\epsilon_F} + \frac{|V_{sd}|^4 n_s(\epsilon_F) \left\{ \frac{\partial}{\partial \epsilon} \frac{|G_{d\sigma}(\epsilon)|}{5 n_{d\sigma}(\epsilon)} \right\}}{|V_{sd}|^4 \frac{|G_{d\sigma}(\epsilon_F)|^2}{5 n_{d\sigma}(\epsilon_F)} n_s(\epsilon_F) + |V_{sd}|^2} \quad (48)$$

Quite similarly to the paramagnetic case the first term of (48) can be written as :

$$\frac{\partial}{\partial \epsilon} \left\{ \log \left| \frac{\partial \delta_{\sigma}(\epsilon, V_{dd}^{\sigma})}{\partial V_{dd}^{\sigma}} \right| \right\}_{\epsilon_F} = - \sqrt{\frac{1}{n_{d\sigma}^2(\epsilon_F)} \left[\frac{1}{\pi^2} \left(\frac{dF_{d\sigma}}{d\epsilon} \right)^2 + \left(\frac{d n_{d\sigma}}{d\epsilon} \right)^2 \right]} \sin \left(\frac{2\pi Z_{\sigma}}{5} - \theta_{p\sigma} \right) \quad (49)$$

the phase angle being defined by :

$$\operatorname{tg} \theta_{p\sigma} = \frac{\pi d n_{d\sigma} / d\epsilon(\epsilon_F)}{dF_{d\sigma} / d\epsilon(\epsilon_F)} \quad (50)$$

IV. GENERAL DISCUSSION OF THE SPECIFIC HEAT.

a) PARTICULAR FORMS OF THE $n_d(\epsilon, \Gamma)$ function.

In this part we discuss the contribution to the changes in specific heat associated with some special forms of the $n_d(\epsilon, \Gamma)$ function. We consider the following cases :

i) The $n_d(\epsilon, \Gamma)$ function has a discontinuity at the top of the band.

ii) Special forms of $n_d(\epsilon, \Gamma)$ for which a virtual bound state may occur.

Some applications of this discussion will be made in paragraph V.

i) Discontinuity at the top of the Γ sub-band.

Let's consider the $n_d(\epsilon, \Gamma)$ function depicted in fig. (1), which is characterized by $n_d(\epsilon_{\text{top}}, \Gamma) \neq 0$. (the energy dependence of it for other energies being unimportant for the discussion). An example of this situation is found in Fletcher's band calculation [10] of Nickel. The origin of the particular behaviour of the density of states in this calculation is that the constant energy surface $\epsilon_{\text{top}} = \epsilon(k)$ is reduced to the diagonals of the square faces of the f.c.c. Brillouin zone.

The essential effect of the discontinuity in $n_d(\epsilon, \Gamma)$ is to produce a logarithmic divergence in its Hilbert transform at $\epsilon = \epsilon_{\text{top}}$, so that for energies close to ϵ_{top} one has :

$$F_d(\epsilon, \Gamma) = A \log |\epsilon - \epsilon_{\text{top}}| \quad (51)$$

where A is a position constant. (cf. fig. 1).

This logarithmic divergence plays an essential role in the behaviour of the phase shift as a function of energy.

In fact, the condition for the occurrence of a bound state is to have a solution of

$$1 - V_{dd}(\Gamma) F_d(\epsilon_0, \Gamma) = 0 \quad (52)$$

such that $\epsilon_0 > \epsilon_{top}$.

From (51) it follows that, for any potential strength, there are two solutions of (52), one of them occurring always for $\epsilon > \epsilon_{top}$. Consequently, even for very small repulsive perturbations, a bound state is extracted from the $n_d(\epsilon, \Gamma)$ sub-band.

The phase shift $\delta_d(\epsilon, \Gamma)$ is there equal to $-\pi$ for $\epsilon = \epsilon_{top}$, and it can be shown from (7) that $\frac{\partial}{\partial \epsilon} \delta_d(\epsilon_{top}, \Gamma) = -\infty$.

It follows also from (7) that for increasing $\epsilon_{top} - \epsilon$, $|\delta_d(\epsilon, \Gamma)|$ decreases monotonically to zero. (cf.fig.1).

From the behaviour of the phase shift one deduces how the density of states is changed by the perturbation using

$$\Delta n_d(\epsilon, \Gamma) = \frac{n\Gamma}{\pi} \frac{\partial}{\partial \epsilon} \delta_d(\epsilon, \Gamma).$$

For all potential values, the slope of the phase shift is negative and is a monotonically decreasing function of energy as illustrated in fig.(1).

The contribution to the specific heat associated with this sub-band is then always negative and becomes stronger the closer the Fermi level is to the top of the Γ sub-band.

This example provides a clear proof of the failure of the rigid band model for some band structures (cf.fig.1).

Even for small perturbations, the results are completely different from those calculated by the rigid band model. We want to remark that, in cases where the discontinuity is replaced by a very rapid increase of the $n_d(\epsilon, \Gamma)$ function near ϵ_{top} , this type of behaviour is still observed.

In fact the logarithmic divergence (38) is replaced by a large value of the $F_d(\epsilon, \Gamma)$ function at $\epsilon = \epsilon_{top}$, and for physically interesting values of the potential the same discussion can be reproduced.

ii) Virtual bound states.

Suppose one has a band structure such that $n_d(\epsilon, \Gamma)$ behaves like $(\epsilon_{\text{top}} - \epsilon)^{n/2}$ ($n = 3, 5, \dots$) around ϵ_{top} , and consequently such that $\frac{d}{d\epsilon} n_d(\epsilon_{\text{top}}, \Gamma) = 0$.

In this situation, for strong enough perturbations, a virtual bound state of Γ symmetry is produced by the localized perturbation {11}.

In fact, for these band structures, $\frac{dF}{d\epsilon}(\epsilon_{\text{top}}, \Gamma) < 0$, and consequently for strong enough perturbations one has two solutions of (52) within the band, one of them being close the top of the band. (cf.fig.2). Then the phase shift increases rapidly from zero at the top of the band (in such a way that $\frac{d\delta}{d\epsilon}(\epsilon_{\text{top}}, \Gamma) = 0$) to reach values near $-\pi$ for energies close to ϵ_{top} (cf.fig.2) after which it decreases slowly to zero. The change in density of states associated with this behaviour of the phase shift is illustrated in fig.3.

The center of this resonance peak is at the energy ϵ_c such that $\frac{\partial^2}{\partial \epsilon^2}(\epsilon_c, \Gamma) = 0$, and the peak contains around n_Γ states of Γ symmetry.

For potentials strong enough to repel a bound state, the phase shift starts from $-\pi$ at $\epsilon = \epsilon_{\text{top}}$ (again with $\frac{d\delta}{d\epsilon}(\epsilon_{\text{top}}, \Gamma) = 0$) and goes to zero slowly as $\epsilon_{\text{top}} - \epsilon$ increases (cf.fig.2).

Finally for weak perturbations, such that there is no solution of (39), $|\delta_d(\epsilon, \Gamma)|$ is always lower than $\pi/2$. The phase shift starts from zero at $\epsilon = \epsilon_{\text{top}}$, decreases slowly to a minimum value $\delta(\epsilon_m, \Gamma)$ such that $|\delta(\epsilon_m, \Gamma)| < \frac{\pi}{2}$, and then goes slowly to zero.

The schematic behaviour of $\frac{d}{d\epsilon} \delta(\epsilon, \Gamma)$ is shown in fig.(2) for several values of the potential as a function of the energy.

The dependence on the impurity excess charge Z of the change in state density introduced by the virtual bound state is shown schematically in fig.(4).

For increasing potential strength $V(\Gamma)$ (with increasing excess charge) the center of the resonant state moves towards the top of the band and its width decreases. (cf.fig.2). Then for given host metal (fixed ϵ_F) one expects that the change $\Delta_n(\epsilon_F)$ would pass through a maximum, decreases to zero and become then negative.

The zero of $\Delta_n(\epsilon_F)$ occurs when the minimum of the phase shift as a function of energy coincides with ϵ_F (cf.fig.2).

An expression for the corresponding charge as a function of the band structure and the position of the Fermi level is given in Appendix II.

b) GENERAL DISCUSSION OF EQUATION (14).

The purpose of this discussion is to predict qualitatively how $\frac{\Delta\gamma}{\Delta c}(c=0)$ varies with Z as a function of the parameter $R(\epsilon_F)$ defined by (15).

The interest of doing this is twofold . For paramagnetic metals it can provide a qualitative knowledge of the band parameters at the Fermi level if experimental data is available for several alloys of the same host element. For ferromagnetic alloys, following the discussion of IIIb) it provides the general behaviour of the contribution of each spin sub-band to the total change in specific heat.

We study separately several cases.

i) The Fermi level lies at the bottom of a "valley" of the density of states ($\frac{dn}{d\epsilon}(\epsilon_F) = 0$).

In this case expression (13) becomes :

$$\frac{\Delta\gamma}{\Delta c}(c=0) = - \frac{5\alpha \sin^2 \frac{\pi Z}{10}}{\pi^2 n(\epsilon_F)} \frac{dF}{d\epsilon}(\epsilon_F) \quad (53)$$

It should be noted that expression (53) and all the others below are valid only for $|Z| < |Z_m|$ where Z_m is the maximum displaced charge (attracted or repelled) by the impurity, corresponding to an infinitely attractive or repulsive potential.

From (53) it follows that the sign of $\frac{\Delta\gamma}{\Delta c}(c=0)$ is independent of the value and sign of Z , $\frac{\Delta\gamma}{\Delta c}$ varying as a sine squared function of Z (cf.fig.5).

Finally the sign of $\frac{\Delta\gamma}{\Delta c}$ is only determined by the sign of $\frac{d_F}{d\epsilon}(\epsilon_F)$.

Consequently if one knows for some reason that the slope of the density of states at the Fermi level is zero, it is possible to determine experimentally $\frac{d_F}{d\epsilon}(\epsilon_F)$, which depends on the general behaviour of the density of states as a function of energy. Examples of this situation are given in figs.(6) and (7). In fig. (6), for $\epsilon_F = \epsilon_0$ one has the case where $\frac{\Delta\gamma}{\Delta c} < 0$ because $\frac{d_F}{d\epsilon}(G_F) > 0$ and in fig.(7) for $\epsilon_F = \epsilon_1$ one has $\frac{\Delta\gamma}{\Delta c}(c=0) > 0$ since $\frac{d_F}{d\epsilon}(\epsilon_F) < 0$.

ii) The Fermi energy is such that $\frac{d_F}{d\epsilon}(\epsilon_F) = 0$.

Then (14) becomes :

$$\frac{\Delta\gamma}{\Delta c}(c=0) = \frac{5\alpha \sin \frac{\pi Z}{5}}{2\pi n(\epsilon_F)} \frac{d}{d\epsilon} n(\epsilon_F) , \quad |Z| < |Z_m| \quad (54)$$

This situation is different from i) in two aspects. Firstly the changes in specific heat have opposite sign for attractive and repulsive impurities, secondly, for the cases where the band structure contains only few holes and $|Z_m| > 5$, one observes a change in sign of $\frac{\Delta\gamma}{\Delta c}$ for impurities such that $|Z| > 5$. (cf.fig.8).

An example of such a situation is given in fig.(9) for a band structure with a peak of density of states and for $\epsilon_F = \epsilon_2$. The case of fig.(7) can be used also as illustrative of this case. ($\epsilon_F = \epsilon_3$ and $\epsilon_F = \epsilon_4$) but the change in sign for the repulsive impurities would be rather difficult to observe since $Z_m \approx -5$.

iii) Discussion of the general case ($\frac{dn_d}{d\epsilon}(\epsilon_F) \neq 0$ and $\frac{dF_d}{d\epsilon}(\epsilon_F) \neq 0$.)

Several possibilities can be considered according to the sign of each one of these quantities. In order to simplify the discussion, expression (14) can be rewritten as :

$$\frac{\Delta Y}{\Delta c}(c=0) = \frac{5\alpha}{2\pi^2} \frac{1}{n_d(\epsilon_F)} \frac{dF_d}{d\epsilon}(\epsilon_F) \sin \frac{\pi Z}{5} \left\{ \frac{\pi}{R(\epsilon_F)} - \operatorname{tg} \frac{\pi Z}{10} \right\} \quad (55)$$

The first thing to be remarked is that for $Z = \pm 5$, (55) becomes :

$$\frac{\Delta Y}{\Delta c}(c=0) = - \frac{5\alpha}{2\pi^2} \frac{1}{n_d(\epsilon_F)} \frac{dF_d}{d\epsilon}(\epsilon_F) \quad (56)$$

Thus the sign of $\frac{dF_d}{d\epsilon}(\epsilon_F)$ specifies completely the sign of $\frac{\Delta Y}{\Delta c}$ for these cases (for usual metals $Z = -5$ is an important case, since there are only a few holes in the d-band and large values of Z can be screened by a localized potential).

The sign of $\frac{\pi}{R(\epsilon_F)} - \operatorname{tg} \frac{\pi Z}{10}$ is shown in fig.(10) as a function of Z and $R(\epsilon_F)$.

Combining these results several possibilities occur :

$$\text{iii-1) } \frac{dn_d}{d\epsilon}(\epsilon_F) < 0 \text{ and } \frac{dF_d}{d\epsilon}(\epsilon_F) < 0.$$

An example of this case is shown in fig.(9) for $\epsilon_F = \epsilon_5$.

For repulsive impurities ($Z < 0$), $\frac{\Delta Y}{\Delta c}$ is positive for all values of Z such that $Z_1 < Z < 0$ (cf.fig.10), Z_1 , being defined by :

$$Z_1 = -10 + \frac{10}{\pi} \operatorname{arctg} \left\{ \frac{\pi}{R(\epsilon_F)} \right\} \quad (57)$$

For $Z = Z_1$, the charge in specific heat is zero, and for $Z < Z_1$ it follows that $\frac{\Delta Y}{\Delta c} < 0$. It is to be noted that $|Z_1|$ is always larger than $+5$ because the argument of the arctangent can vary only between 0 and $+\infty$. In conclusion one observes negative changes in the specific heat only for strongly repulsive impurities.

In order to get consistency one should have $Z_m < Z_1$ and

consequently the criterion to observe $\frac{\Delta\gamma}{\Delta c} < 0$ for repulsive impurities is (assuming that $F_d(\epsilon_F) > 0$) :

$$\frac{\pi n_d(\epsilon_F)}{F_d(\epsilon_F)} < \frac{\pi}{R(\epsilon_F)} \quad (58)$$

For attractive impurities ($Z > 0$), $\frac{\Delta\gamma}{\Delta c}$ is negative for $0 < Z < Z_2$, Z_2 being defined by $Z_2 = Z_1 + 10$ and positive for $Z > Z_2$.

The schematic behaviour of the specific heat in this case is shown in fig.(11).

$$\text{iii-2) } \frac{d n_d}{d \epsilon}(\epsilon_F) > 0 \text{ and } \frac{d F_d}{d \epsilon}(\epsilon_F) > 0.$$

An example of this situation is given in fig.(6) for $\epsilon_F = \epsilon_6$.

The same discussion as in iii-1) can be reproduced here except for the sign which should be changed everywhere.(cf.fig.12).

$$\text{iii-3) } \frac{d n_d}{d \epsilon}(\epsilon_F) < 0 \text{ and } \frac{d F_d}{d \epsilon}(\epsilon_F) > 0.$$

Fig.(6) still provides an example for this case if $\epsilon_F = \epsilon_7$.

For repulsive impurities, $\frac{\Delta\gamma}{\Delta c}$ is positive for $Z_3 < Z < 0$, Z_3 still being given by (57) (cf.fig.10). It should be remarked that $|Z_3|$ now is always less than 5 because the argument of the arctangent can vary only between 0 and $-\infty$.

Again for $Z = Z_3$, $\frac{\Delta\gamma}{\Delta c}$ vanishes and for $|Z| > Z_3$ it becomes negative.

We want to stress that this kind of behaviour is observed for any positive value of $\frac{\pi n_d(\epsilon_F)}{F_d(\epsilon_F)}$, because $Z_m = -\frac{10}{\pi} \text{ arctg} \left\{ -\frac{\pi n_d(\epsilon_F)}{F_d(\epsilon_F)} \right\}$ is always smaller than -5 .

Finally for attractive impurities, $\frac{\Delta\gamma}{\Delta c}$ is negative for $0 < Z < Z_4$ (cf.fig.10), and positive for $Z > Z_4$. The schematic behaviour of $\frac{\Delta\gamma}{\Delta c}$ in this case is shown in fig.(13).

$$\text{iii-4) } \frac{d n_d}{d \epsilon}(\epsilon_F) > 0 \text{ and } \frac{d F_d}{d \epsilon}(\epsilon_F) < 0.$$

The same discussion as in iii-3) except for a change in sign everywhere (cf.fig.14).

V. RESULTS AND DISCUSSION

The parameters which determine the behaviour of the change in electronic specific heat per added impurity are very dependent on the exact form of the density of states curve of the host metal and on the position of the Fermi level, even for a simple host density of states curve. An alloy which already contains a few percent of impurity will not respond in the same way as would the host metal to the addition of further impurities. Because of this one would expect that the change in specific heat for a given impurity in a given host would not be linear in impurity concentration beyond possibly 1 or 2 percent. There are in addition often structure, ordering, and magnetic effects as concentration increases, so the specific heat will generally be a complicated function of concentration, as is indeed found experimentally. The expressions given above can really only be tested with low impurity concentration results for a series of different impurities dissolved in the same host metal ; the values for such a series should follow the expression given above with Z the only parameter which changes.

An excellent study of this type has been carried out by Shinozaki and Arrott on iron based dilute alloys {1} . Their results for transition impurities are shown in figure 14. Unfortunately, as iron is a ferromagnetic metal there are too many free parameters for it to be possible to check the model convincingly. However, using the expression of section IV, the results would be consistent with a band structure which has the following properties :

At $E_{F\downarrow}$, dn/dE small, dF/dE negative

At $E_{F\uparrow}$, dn/dE large and negative, dF/dE small.

A density of states curve, with the positions of the Fermi levels for the two spin directions which fulfills these conditions is given in figure 14 ; the numerical results corresponding to this are shown in figure 15. It is satisfactory that reasonable agreement can be reached with approximately the same density of states curve as that generally used to explain the magnetic properties of iron.

For Nickel containing transition impurities, Gupta, Cheng and Beck {12} give results for specific heat changes, though unfortunately only for rather high minimum concentrations. The results are shown in figure 16. Ferromagnetic nickel is usually assumed to have a completely filled spin $\uparrow$ band, and 0.6 holes in the spin $\downarrow$ band. From Fletcher's calculation of the band structure of nickel {10} one expects a discontinuity in $n(E)$ at the top of each λ band. It follows from the general discussion of paragraph IIIa) that even for a very small perturbation a bound state is repelled from either of the sub-bands. But as the top of the spin $\uparrow$ band is lower than E_F , a minimum strength $V_{\min}^{\uparrow}$ of the perturbation is needed to make the spin $\uparrow$ bound state cross the Fermi level. We will first discuss the case $V^{\uparrow} < V_{\min}^{\uparrow}$. According to {7}, this is the case of Ni with Fe, Co or Mn. The change of spin $\uparrow$ density of states remains zero, as the spin $\uparrow$ bound state lies below the Fermi level, but for spin $\downarrow$ the bound state leaving the $\downarrow$ band means that the density of states at E_F $\downarrow$ drops. This is consistent with the observed negative values of $d\gamma/dc$ for NiFe, NiCo. To explain a positive value for NiMn, we need to refine the model. The s-d mixing in the spin $\uparrow$ direction will broaden the spin $\uparrow$ bound state, by mixing it with the

Spin $\uparrow$ s electrons to produce something similar to a virtual bound state as it occurs in normal metal alloys with transition elements. This effect produces a positive contribution to the density of states at the Fermi level, which is large when the centre of the bound state is near E_F . A calculation of this effect is not within the scope of this paper, as s-d mixing should be included consistently from the beginning.

The case of Pd alloys should be handled very carefully. Firstly it is known that very pure samples of these metals should be used in order to avoid spurious effects of impurities like Fe. In this situation the available results should be regarded with a certain caution because the effects of these impurities could mask completely the effects of the dissolved elements that one wants to observe.

Even in the case of very pure samples, the electron-electron interactions seem to play an important role in Pd alloys because Pd itself is near to being ferromagnetic. If these effects are not taken into account (or at least estimated) the one electron analysis made in this paper may be misleading.

Results on resistivities and thermoelectric power are very sparse, except for iron and nickel hosts. But because these are ferromagnetics, the transport properties are expressed in a complicated form, and again the data cannot be used to test very convincingly the expressions of the model.

APPENDIX I

Virtual bound state : variation of the minimum of $\delta(\epsilon, \Gamma)$ with the potential strength.

Consider the density of states as behaving like $\alpha(\epsilon_t - \epsilon)^{n/2}$ ($n = 3, 5, \dots$) around the top of the band ($\epsilon = \epsilon_{\text{top}}$). One knows that in this situation a v.b.s. may be produced by the perturbation $\{1\}$.

Take $V(\Gamma)$ satisfying the following condition :

$$\frac{1}{V(\Gamma)} < \max F_d(\epsilon, \Gamma) = F_d(\epsilon^m, \Gamma) \quad (\text{A1})$$

where ϵ^m is the energy corresponding to this maximum of $F_d(\epsilon, \Gamma)$.

In this case one has certainly two solutions of the equation (cf. fig. 2)

$$1 - V(\Gamma) F_d(\epsilon, \Gamma) = 0 \quad (\text{A2})$$

let ϵ_0 be the solution of (A2) such that $\epsilon^m > \epsilon_0$ (cf. fig. 2)

The phase shift $\delta(\epsilon, \Gamma) = \arctg \left\{ - \frac{\pi n_d(\epsilon, \Gamma)}{F_d(\epsilon, \Gamma) - \frac{1}{V(\Gamma)}} \right\}$ is minimum when

$$g(\epsilon) = \frac{\pi n_d(\epsilon, \Gamma)}{F_d(\epsilon, \Gamma) - \frac{1}{V(\Gamma)}} \text{ is maximum (note that for } \epsilon^m < \epsilon < \epsilon_0, g(\epsilon) > 0)$$

Let ϵ_m be the energy value that makes $g(\epsilon)$ maximum ; ϵ_m should satisfy :

$$\frac{dg}{d\epsilon} = \pi \frac{\left[F_d(\epsilon_m, \Gamma) - \frac{1}{V(\Gamma)} \right] \frac{dn_d}{d\epsilon} - n_d(\epsilon_m, \Gamma) \frac{dF_d}{d\epsilon}(\epsilon_m, \Gamma)}{\left[F_d(\epsilon_m, \Gamma) - \frac{1}{V(\Gamma)} \right]^2} = 0$$

or

$$\left[F_d(\epsilon_m, \Gamma) - \frac{1}{V(\Gamma)} \right] \frac{dn_d}{d\epsilon}(\epsilon_m, \Gamma) - n_d(\epsilon_m, \Gamma) \frac{dF_d}{d\epsilon}(\epsilon_m, \Gamma) = 0 \quad (\text{A3})$$

The function $F_d(\epsilon, \Gamma)$ is such that (as verified by numerical calculations) $\frac{dF_d}{d\epsilon}(\epsilon, \Gamma) \approx \text{const.}$ between ϵ^m and ϵ_{top} . Then one may write for this energy interval :

$$F_d(\epsilon_m, \Gamma) = F_d(\epsilon_o, \Gamma) + \frac{dF_d}{d\epsilon}(\epsilon_o, \Gamma)(\epsilon_m - \epsilon_o) \quad (\text{A4})$$

Equation (A3) becomes then :

$$(\epsilon_m - \epsilon_o) \frac{dF_d}{d\epsilon}(\epsilon_o, \Gamma) \frac{dnd}{d\epsilon}(\epsilon_m, \Gamma) = n_d(\epsilon_m, \Gamma) \frac{dF_d}{d\epsilon}(\epsilon_m, \Gamma)$$

or

$$\frac{1}{\epsilon_m - \epsilon_o} = \frac{1}{n_d(\epsilon_m, \Gamma)} \frac{dnd}{d\epsilon}(\epsilon_m, \Gamma) \quad (\text{A5})$$

Last step follows from the fact that $\frac{dF_d}{d\epsilon}(\epsilon_o, \Gamma) \approx \frac{dF_d}{d\epsilon}(\epsilon_m, \Gamma)$

Using the density of states $\alpha(\epsilon_t - \epsilon)^{n/2}$, equation (A6) becomes :

$$\frac{\epsilon_{\text{top}} - \epsilon_o}{\epsilon_{\text{top}} - \epsilon_m} = \frac{n - 2}{n} \quad (\text{A6})$$

Expression (A6) connects the energy value corresponding to the minimum of the phase shift to the energy for which $|\delta(\epsilon, \Gamma)| = \pi/2$, thus providing the variation of the width of the virtual state with the potential strength.

It shows also that for a given value of $V(\Gamma)$ the width decreases with increasing values of n . This confirms for tightly bound electrons the classical result of the free-electron case : the width of the virtual bound states decreases with the increasing angular momentum ($p, d, f, \text{etc.}$).

APPENDIX II.

Virtual bound state : value of the screening charge for which
 $\frac{\Delta n}{\Delta c}(c=0) = 0.$

Essentially one wants to calculate for which value of Z ,
 $\epsilon_m = \epsilon_F$ (cf. appendix I). The relation (A6) becomes in this case :

$$\frac{\epsilon_{top} - \epsilon_o}{\epsilon_{top} - \epsilon_F} = \frac{n - 2}{n} \quad (B1)$$

Using the same arguments of appendix I one has :

$$F_d(\epsilon, \Gamma) = F_d(\epsilon_{top}, \Gamma) + \frac{dF_d}{d\epsilon}(\epsilon_{top}, \Gamma)(\epsilon - \epsilon_{top})$$

(B2)

and in particular :

$$F_d(\epsilon_o, \Gamma) = F_d(\epsilon_{top}, \Gamma) + \frac{dF_d}{d\epsilon}(\epsilon_{top}, \Gamma)(\epsilon_o - \epsilon_{top})$$

where ϵ_o is again the solution of $1 - V_o(\Gamma)F_d(\epsilon_o, \Gamma) = 0$ such that
 $\epsilon_m > \epsilon_o$ and $V_o(\Gamma)$ is the value of the potential for which (B1) is
satisfied.

From (B2) one has :

$$\frac{1}{V_o(\Gamma)} - F_d(\epsilon_{top}, \Gamma) = \frac{dF_d}{d\epsilon}(\epsilon_{top}, \Gamma)(\epsilon_o - \epsilon_{top}) \quad (B3)$$

The charge displaced by $V_o(\Gamma)$ is given by :

$$Z_o = - \frac{n_\Gamma}{\pi} \arctg \left\{ \frac{\pi n_d(\epsilon_F, \Gamma)}{\frac{1}{V_o(\Gamma)} - F_d(\epsilon_F, \Gamma)} \right\} =$$

$$- \frac{n_\Gamma}{\pi} \arctg \left\{ \frac{n_d(\epsilon_F, \Gamma)}{\frac{1}{V_o(\Gamma)} - F_d(\epsilon_{top}, \Gamma) + F_d(\epsilon_{top}, \Gamma) - F_d(\epsilon_F, \Gamma)} \right\} \quad (B4)$$

The denominator can be rewritten using (B1), (B2) and (B3) :

$$\frac{1}{V_0(\Gamma)} - F_d(\epsilon_{\text{top}}, \Gamma) + F_d(\epsilon_{\text{top}}, \Gamma) - F_d(\epsilon_F, \Gamma) = \frac{2}{n} \frac{dF_d}{d\epsilon}(\epsilon_{\text{top}}, \Gamma)(\epsilon_{\text{top}} - \epsilon_F) \quad (\text{B5})$$

For the density of states $n_d(\epsilon, \Gamma) = \alpha(\epsilon_{\text{top}} - \epsilon)^{n/2}$, (B4) becomes :

$$Z_0 = \frac{n_\Gamma}{\pi} \arctg \left\{ \frac{\pi n \alpha}{2 \frac{dF_d}{d\epsilon}(\epsilon_{\text{top}}, \Gamma)} (\epsilon_{\text{top}} - \epsilon_F)^{n/2-1} \right\} \quad (\text{B6})$$

APPENDIX III.

Variation of the minimum of $\delta(\epsilon, \Gamma)$ for a band with parabolic behaviour near the top.

In this case {11} a solution of $1 - V(\Gamma)F_d(\epsilon, \Gamma) = 0$ within the band is always accompanied by another solution for $\epsilon > \epsilon_{\text{top}}$. Consequently the existence of solutions correspond to the existence of a bound state, and to a monotonic decrease of $|\delta(\epsilon, \Gamma)|$ from π to zero.

Then a minimum of $\delta(\epsilon, \Gamma)$ (and consequently positive changes in the density of states) can occur only for $\frac{1}{V(\Gamma)} > F_d(\epsilon_{\text{top}}, \Gamma)$.

Let's suppose that this condition is fulfilled and define the parameter $x > 0$ by :

$$x = \frac{1}{V(\Gamma)} - F_d(\epsilon_{\text{top}}, \Gamma) \quad (\text{C1})$$

Using a similar reasoning to that of appendix I one has :

$$\frac{1}{V(\Gamma)} - F_d(\epsilon, \Gamma) = x - \frac{dF_d}{d\epsilon}(\epsilon_{\text{top}}, \Gamma)(\epsilon - \epsilon_{\text{top}}) \quad (\text{C2})$$

Again the minimum of the phase shift occurs at the energy ϵ_m solution of :

$$\frac{dn_d}{d\epsilon}(\epsilon_m, \Gamma) \left[\frac{1}{V(\Gamma)} - F_d(\epsilon_m, \Gamma) \right] + n_d(\epsilon_m, \Gamma) \frac{dF_d}{d\epsilon}(\epsilon_m, \Gamma) = 0 \quad (\text{C3})$$

Using (C2) expression (C3) can be rewritten as :

$$x + \frac{d_{Fd}}{d\varepsilon}(\varepsilon_{top}, \Gamma)(\varepsilon_{top} - \varepsilon_m) = - \frac{n_d(\varepsilon_m, \Gamma)}{\frac{d_{nd}}{d\varepsilon}(\varepsilon_m, \Gamma)} \frac{d_{Fd}}{d\varepsilon}(\varepsilon_t, \Gamma) \quad (C4)$$

which for $n_d(\varepsilon, \Gamma) = \alpha(\varepsilon_{top} - \varepsilon)^{1/2}$ becomes :

$$\varepsilon_{top} - \varepsilon_m = \frac{x}{\frac{d_{Fd}}{d\varepsilon}(\varepsilon_{top}, \Gamma)} \quad (C5)$$

Quite similarly to appendix II it can be shown that the displaced charge Z_o for which $\frac{\Delta n}{\Delta c}(c=0) = 0$ is given by :

$$Z_o = - \frac{n_\Gamma}{\pi} \operatorname{arctg} \left\{ \frac{\pi \alpha}{2 \frac{d_{Fd}}{d\varepsilon}(\varepsilon_{top}, \Gamma)} (\varepsilon_{top} - \varepsilon_F)^{-1/2} \right\} \quad (C6)$$

which is exactly (B6) for $n = 1$.

Acknowledgements.

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REFERENCES

- 1) S. SHINAZAKI and A. ARROT, Phys. Rev. 152, 611 (1966).
- 2) N. MOTT, Adv. Phys. Vol. 13, N°51 (1964).
- 3) J. CALLAWAY, J. Math. Phys. 5, 783 (1964).
- 4) F. GAUTIER and P. LENGART, Phys. Rev. 139, A 705 (1965).
- 5) J. KANAMORI, J. Appl. Phys. 36, 929 (1965).
- 6) A.A. GOMES, J. Phys. Chem. Sol. 27, 451 (1966).
- 7) I.A. CAMPBELL and A.A. GOMES, To be published in Proc. Phys. Soc. (London).
- 8) I.A. CAMPBELL and A. FLIRT, To be published.
- 9) J. FRIEDEL, J. Phys. Rad. 11, 37 (1953).
- 10) G.C. FLETCHER, Proc. Phys. Soc. (London) 65, 192 (1952).
- 11) J. FRIEDEL et al. Quantum Theory of atoms, molecules, Solid State Academic Press 1966.
- 12) K.P. GUPTA et al. , J. Phys. Rad. 23, 721 (1962).

FIGURE CAPTIONS

- Fig. 1 - Schematic behaviour of the phase shift and change in density of states for the $n(\epsilon, T)$ function with a discontinuity at the top of the band.
- Fig. 2 - Schematic behaviour of the phase shift in the case where a virtual bound state occurs.
- Fig. 3 - Schematic behaviour of the change in density of states in the virtual bound state case.
- Fig. 4 - Change in density of states at the Fermi level as a function of the screening charge in the case of a virtual bound state (schematic).
- Fig. 5 - Change in electronic specific heat as a function of Z for a band structure such that $\frac{dn_d}{d\epsilon}(\epsilon_F) = 0$ (schematic).
- Fig. 6 - $F_d(\epsilon)$ function for a band structure with a parabolic behaviour near the top of the band (schematic).
- Fig. 7 - $F_d(\epsilon)$ function for two overlapping parabolae (schematic)
- Fig. 8 - Change in electronic specific heat as a function of Z for a band structure such that $\frac{dF_d}{d\epsilon}(\epsilon_F) = 0$ (schematic).
- Fig. 9 - $F_d(\epsilon)$ function for a band structure with a regular peak of density of states (schematic).
- Fig.10 - Z values for which the function $\frac{\pi}{R(\epsilon_F)} - \text{tg} \frac{\pi Z}{10}$ is positive, as a function of $R(\epsilon_F)$ (schematic).
- Fig.11 - Change in electronic specific heat as a function of Z for $R(\epsilon_F) > 0$ and $\frac{dF_d}{d\epsilon}(\epsilon_F) < 0$ (Schematic).
- Fig.12 - Change in electronic specific heat as a function of Z for $R(\epsilon_F) > 0$ and $\frac{dF_d}{d\epsilon}(\epsilon_F) > 0$ (schematic).
- Fig.13 - Change in electronic specific heat as a function of Z for $R(\epsilon_F) < 0$ and $\frac{dF_d}{d\epsilon}(\epsilon_F) > 0$ (schematic).
- Fig.14 - Change in electronic specific heat as a function of Z for $R(\epsilon_F) < 0$ and $\frac{dF_d}{d\epsilon}(\epsilon_F) < 0$ (schematic).
- Fig. 15- Change in electronic specific heat of iron based alloys.
- Fig.16 - Adopted band structure for iron (schematic).
- Fig.17 - Change in electronic specific heat of nickel based alloys.

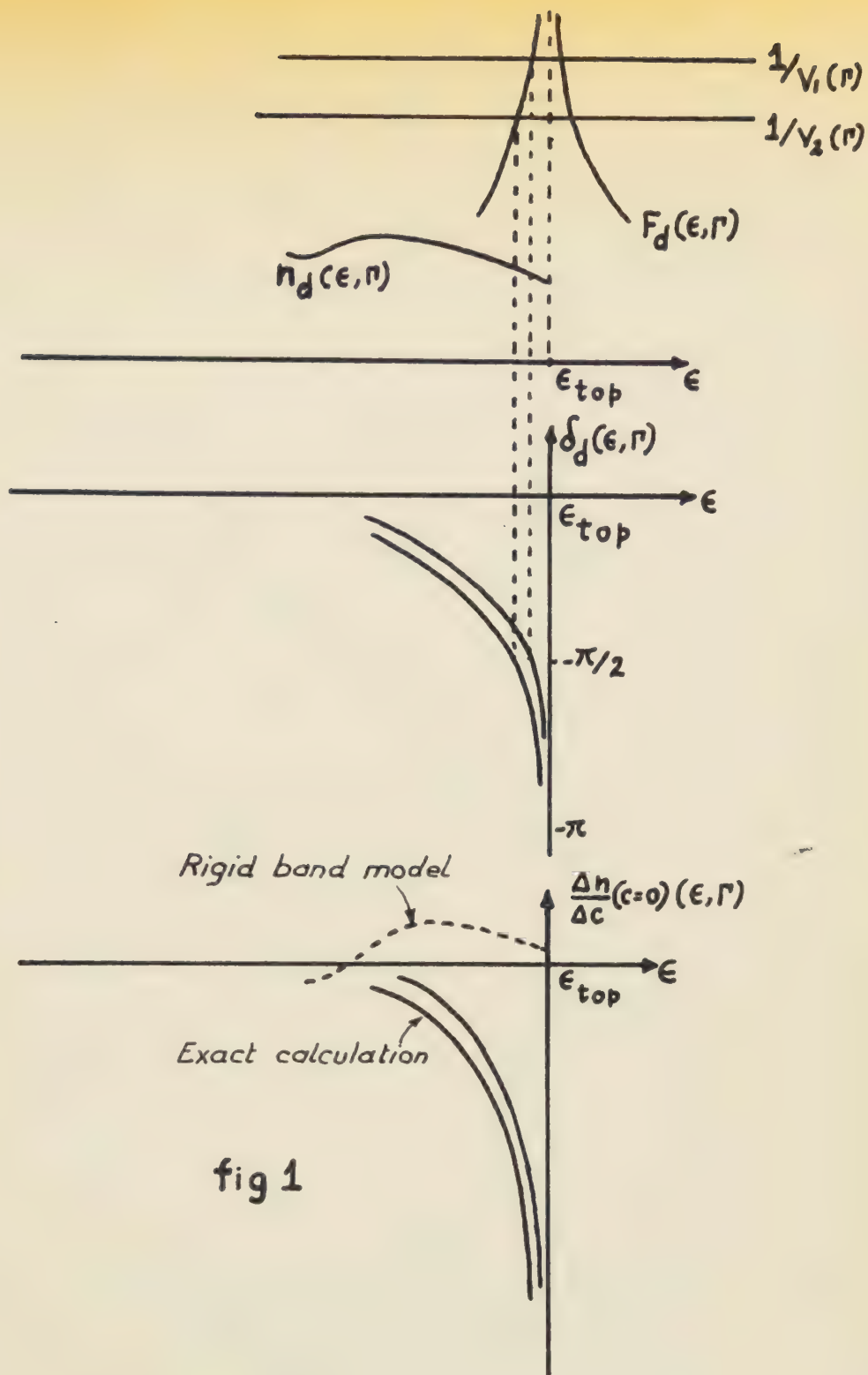


fig 1

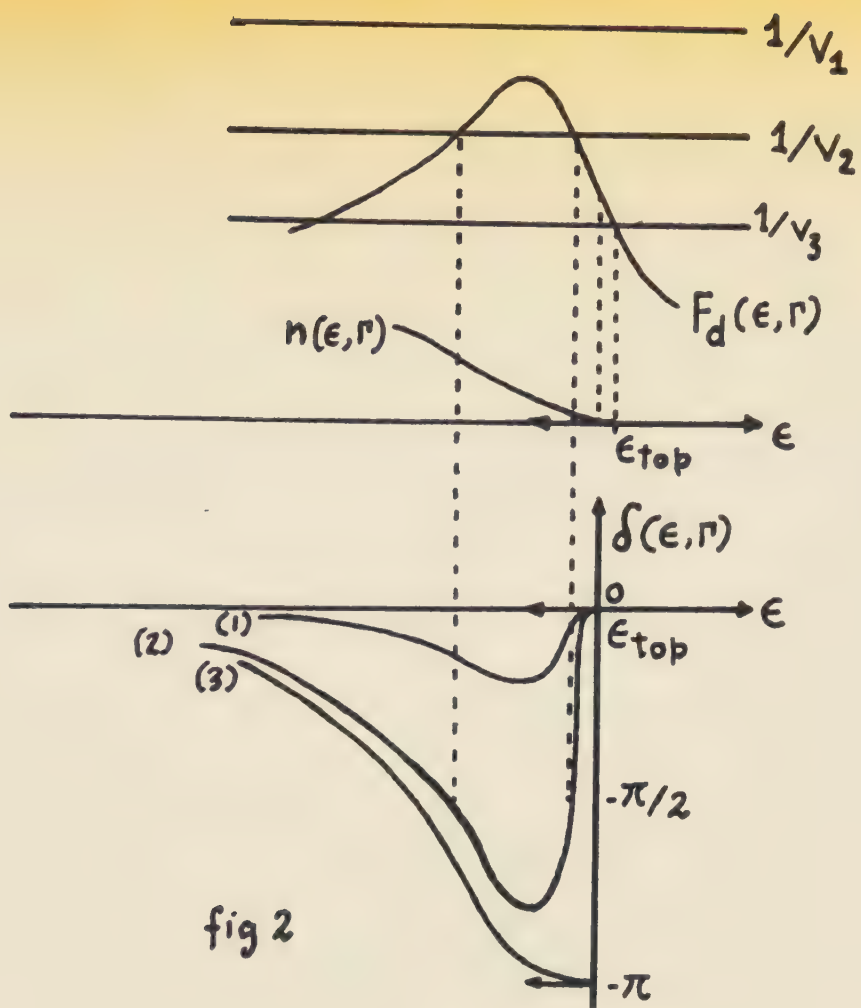


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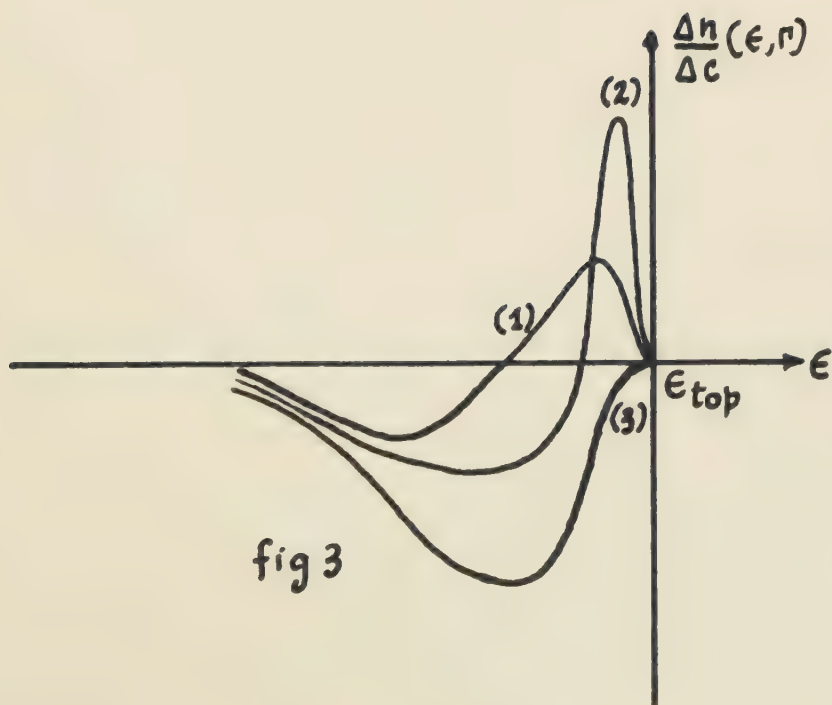


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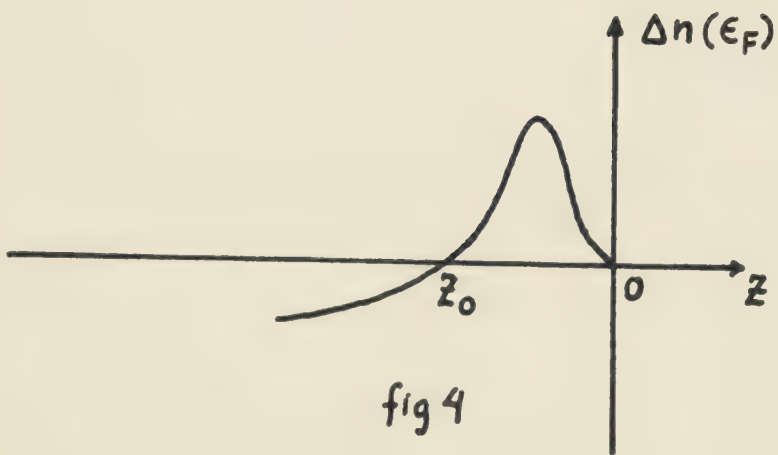


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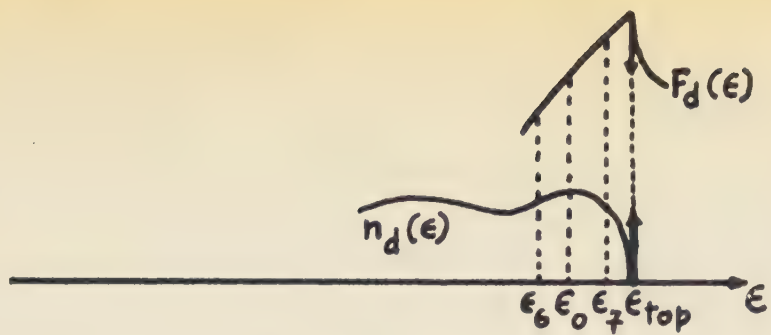


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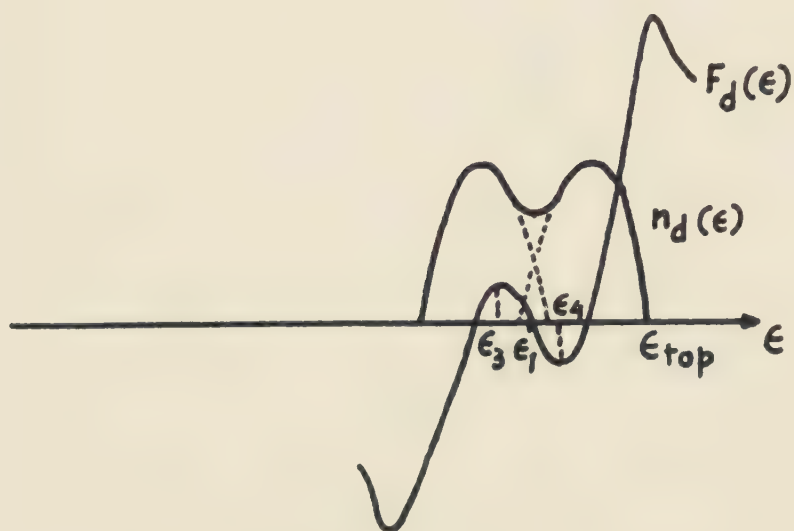


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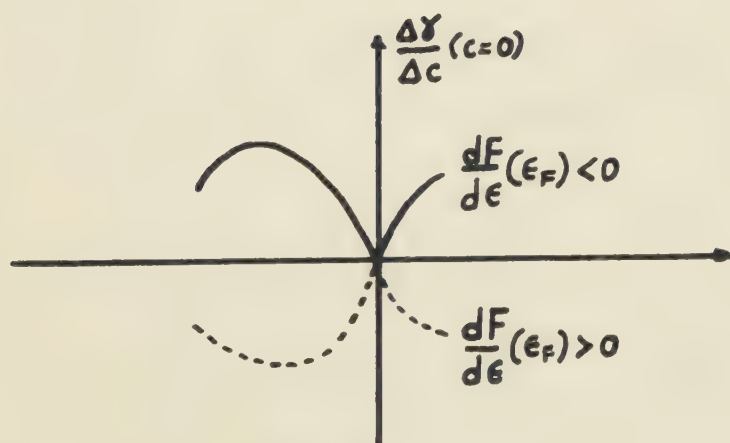


fig 5

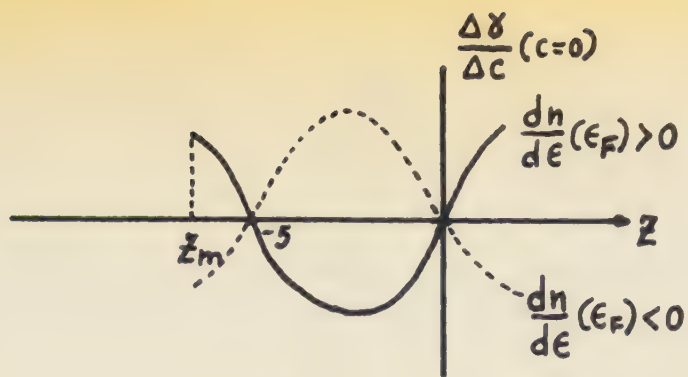


fig 8

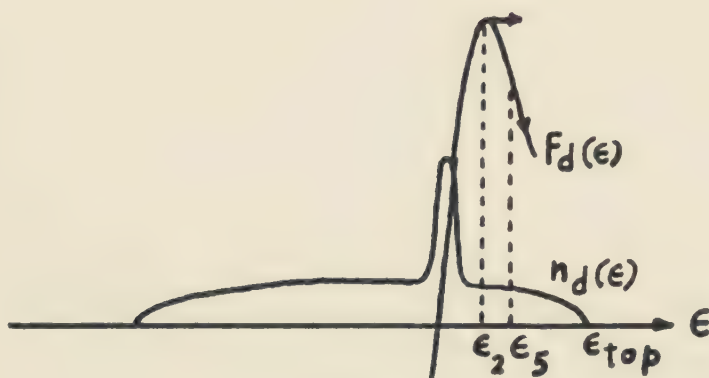


fig 9

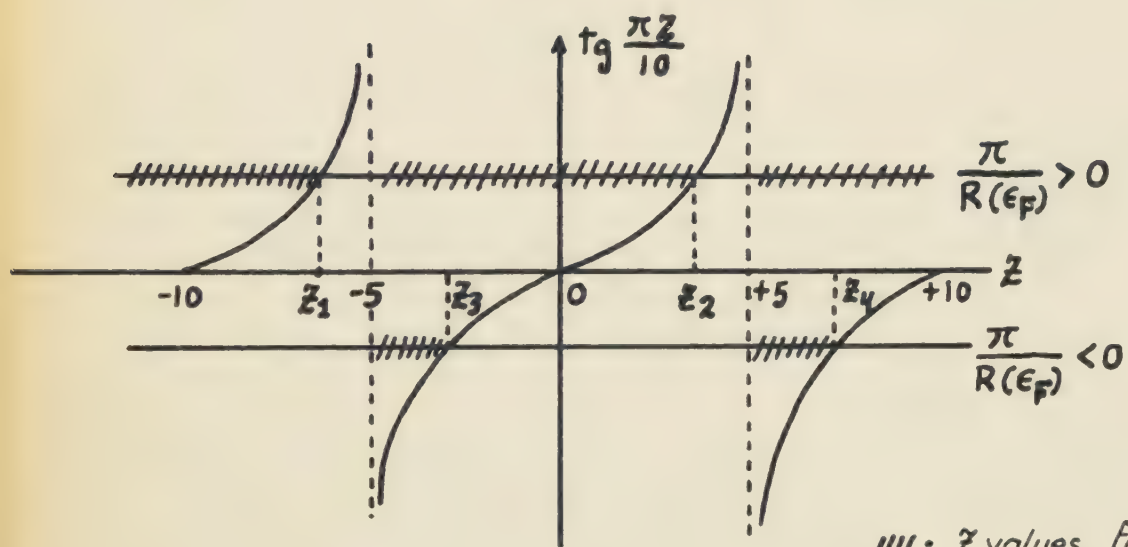


fig 10

////: z values for which $\frac{\pi}{R(\epsilon_F)} - \text{tg} \frac{\pi z}{10} > 0$

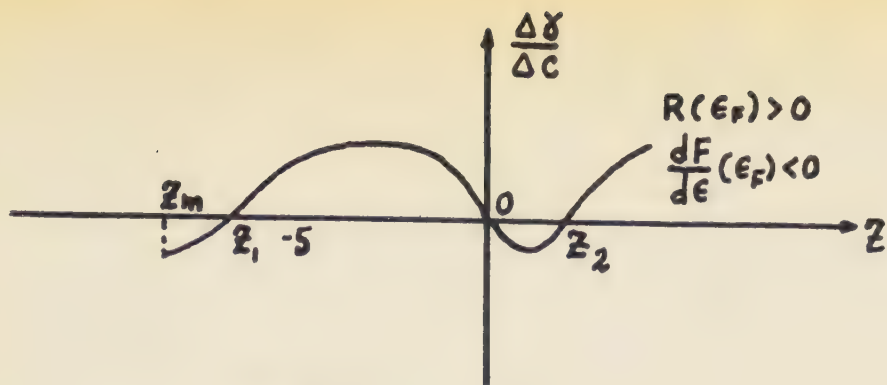


fig 11

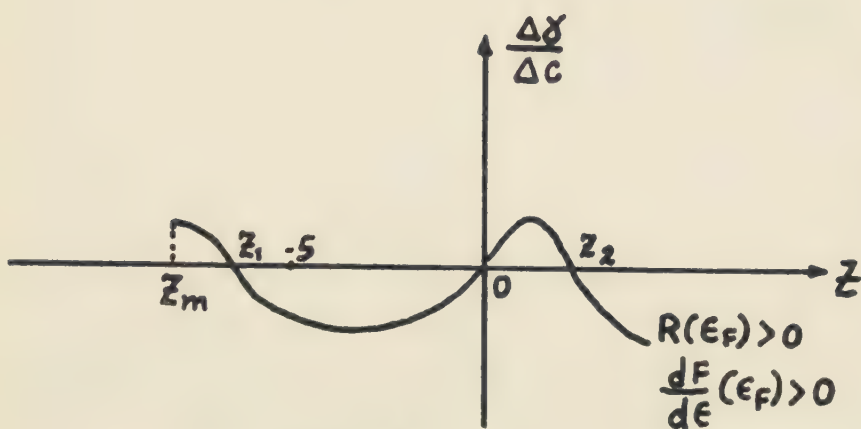


fig 12

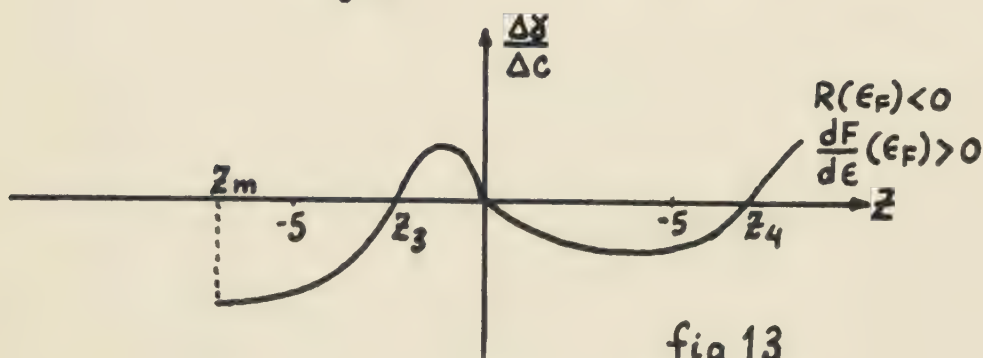


fig 13

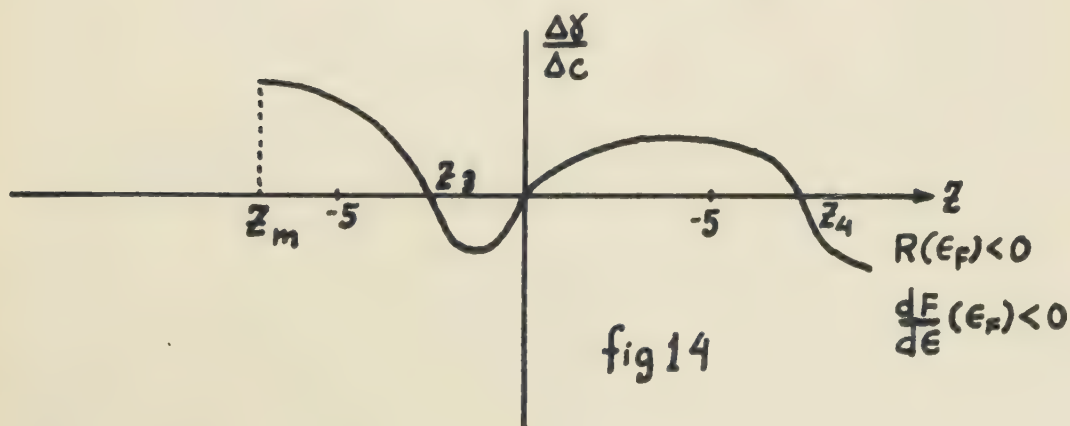


fig 14

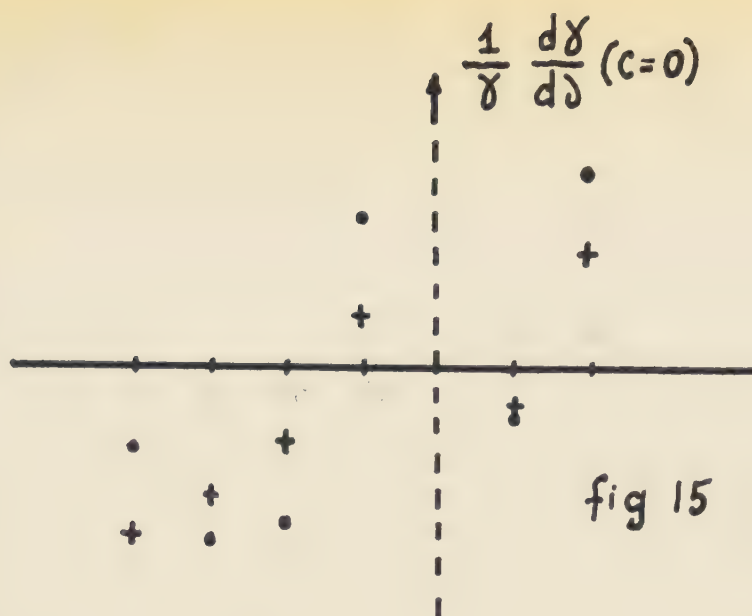


fig 15

• Experimental points
+ From model described in text

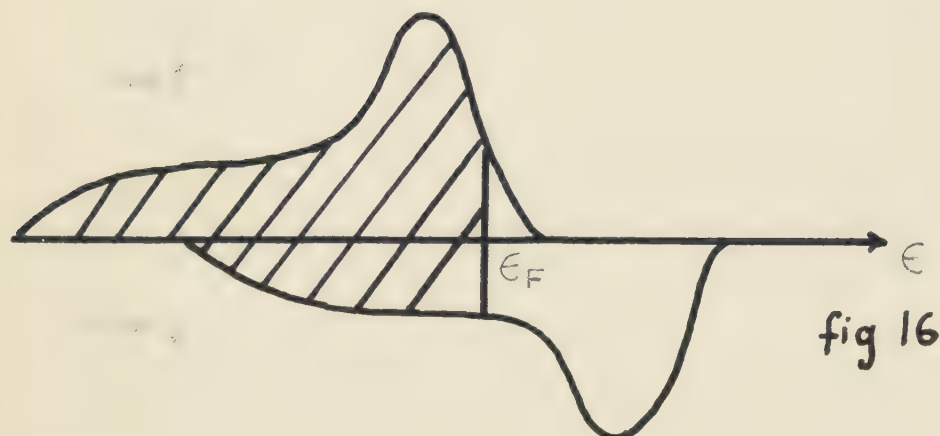


fig 16

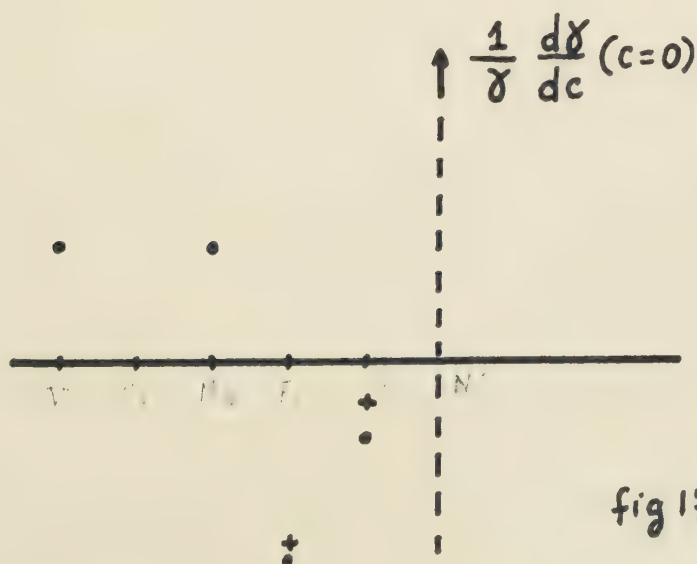


fig 17

CHAPITRE V

DIFFUSION A PLUSIEURS VOIES PAR UN POTENTIEL LOCALISE

to be submitted to Proc. Phys. Soc.

MANY CHANNEL SCATTERING BY A LOCALIZED POTENTIAL
TOTAL DISPLACED CHARGE

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Abstract :

The T matrix formalism is employed to calculate the charge displaced by a localized perturbation acting on a many channel system. The method is applied to the case of s-d mixing produced by an impurity in a metal.

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* This work is a part of a thesis which will be submitted by A.A. Gomes to the Faculté des Sciences d'Orsay, in partial fulfilment of the requirements for the Doctorat ès Sciences Physiques.

INTRODUCTION.

The study of the response of a system to a localized perturbation is in general complicated by the presence of several quantum numbers necessary to describe the system. In fact, the localized perturbation induces transitions between the different quantum states, and the mixing effects are rather difficultly described by standard methods {1}.

In this paper we introduce a T matrix formalism for calculating the total charge displaced in a many channel scattering which leads to a simple way of describing the mixing effects.

These results are then applied to a discussion of the impurity induced s-d mixing effects in transition metals {2} and the spin flip produced by a spin dependent localized perturbation.

I. GENERAL METHOD.

Suppose there is a series of labels $\{\alpha_1, \alpha_2 \dots \alpha_n\}$ which define the scattering channels, and suppose that the problem of scattering by a localized potential V , including mixing terms, has been solved. The $\{T\}$ matrix for the system can then be written

$$\{T\} = \begin{pmatrix} T_{\alpha_1 \alpha_1} & T_{\alpha_1 \alpha_2} & \dots & T_{\alpha_1 \alpha_n} \\ T_{\alpha_2 \alpha_1} & * & & * \\ \vdots & \vdots & & \vdots \\ T_{\alpha_n \alpha_1} & T_{\alpha_n \alpha_2} & \dots & T_{\alpha_n \alpha_n} \end{pmatrix} \quad (1)$$

where the matrix elements are defined by

$$T_{\alpha_i \alpha_j} = \langle \phi_{\alpha_i} | T | \phi_{\alpha_j} \rangle = \langle \phi_{\alpha_i} | V | \psi_{\alpha_j}^+ \rangle$$

where ϕ_{α_i} , $\psi_{\alpha_i}^+$ are the unscattered and scattered wave functions corresponding to channel α_i .

The T matrix can be diagonalized by a unitary transformation U ,

$$\hat{T} = U^{-1} T U \quad (2)$$

where U is difficult to calculate in the general case ; explicit knowledge of U will be shown to be unnecessary for calculating the total charge displaced.

We have

$$T = \begin{pmatrix} T_{\alpha'_1 \alpha'_1} & & & 0 \\ & T_{\alpha'_2 \alpha'_2} & & \\ & & \ddots & \\ 0 & & & T_{\alpha'_n \alpha'_n} \end{pmatrix} \quad (3)$$

and we can define the phase shifts corresponding to the various channels in the diagonal representation by

$$\delta_{\alpha_i} = \arg T_{\alpha_i \alpha_i} \quad (4)$$

with the corresponding displaced charge

$$Z_i' = \frac{1}{\pi} \delta_{\alpha_i} = \frac{1}{\pi} \arg T_{\alpha_i \alpha_i}$$

The total displaced charge

$$\begin{aligned} Z &= \sum_{i'=1}^n Z_i' = \frac{1}{\pi} \sum_{i'=1}^n \arg T_{\alpha_i' \alpha_i'} \\ &= \frac{1}{\pi} \arg \prod_{i'=1}^n T_{\alpha_i' \alpha_i'} \\ &= \frac{1}{\pi} \arg \det \{\tilde{T}\} \end{aligned} \quad (5)$$

as $\tilde{T}$ is diagonal. But the determinant of a matrix is independent of the base set, so

$$Z = \frac{1}{\pi} \arg \det T \quad (6)$$

This result was obtained also by Toulouse {3} using a different and more general approach. In our case the principal aim was to obtain Z in terms of the available {2} matrix elements of T for the s-d mixing in transition metals.

II. EXAMPLES.

This expression is still complicated in the general case ; however we will consider some special cases where there are simplifications.

a) Suppose T can be transformed into a block matrix T_1 .

$$T_1 = \begin{pmatrix} T(P_1) & & 0 \\ \text{---} & T(P_2) & \\ 0 & & T(P_3) \\ & & \ddots \end{pmatrix}$$

Then

$$\begin{aligned} Z &= \frac{1}{\pi} \arg \prod_j \det T(P_j) \\ &= \frac{1}{\pi} \sum_j \arg \det T(P_j) \end{aligned}$$

If the matrix $T(P_j)$ occurs n_j times,

$$Z = \frac{1}{\pi} \sum_j n_j \arg \det T(P_j) \quad (7)$$

b) Suppose channel α_1 is not coupled to channels $\alpha_2 \dots \alpha_n$. This is the case for the usual model in transition metals of an s band independent of a d band.

Then

$$T = \begin{pmatrix} T & 0 & 0 & 0 \\ 1 & 1 & & \\ \hline 0 & & T' & \\ 0 & & & \\ 0 & & & \end{pmatrix}$$

This is a special case of (7)

$$Z = \frac{1}{\pi} \arg T_{\alpha_1 \alpha_1} + \frac{1}{\pi} \arg \det T' \quad (8)$$

c) Suppose there are n independent identical sub-bands

$$T = \begin{pmatrix} T_{\alpha\alpha} & & 0 \\ & T_{\alpha\alpha} & \\ 0 & & T_{\alpha\alpha} \end{pmatrix} \quad (9)$$

and
$$Z = \frac{n}{\pi} \arg T_{\alpha\alpha} \quad (10)$$

Again, for transition metals the initial assumption is frequently that of 5 independent identical d sub-bands.

d) Suppose one channel α_1 is coupled to n others which are independent from each other. (This can be applied directly to a transition metal with an s band coupled to 5 identical d bands).

Any matrix can be transformed into this form ; however only sometimes will this be of physical significance. The determinant becomes

$$\det T = \begin{vmatrix} T_{11} & T_{12} & T_{13} & \cdots & T_{1,n+1} \\ T_{21} & T_{22} & 0 & \cdots & 0 \\ T_{31} & 0 & T_{33} & \cdots & 0 \\ \vdots & 0 & & \ddots & \\ T_{n+1,1} & 0 & 0 & & T_{n+1,n+1} \end{vmatrix} \quad (11)$$

Multiplying through, starting with the top row, gives

$$\det T = \prod_{i=1}^{n+1} T_{ii} - \sum_{j=2}^{n+1} T_{1j} T_{j1} \frac{\prod_{i=2}^{n+1} T_{ii}}{T_{jj}} \quad (12)$$

$$\text{or} \quad \det T = \prod_{i=1}^{n+1} T_{ii} \left[1 - \sum_{j=2}^{n+1} T_{1j} T_{j1} / T_{jj} T_{11} \right] \quad (13)$$

In the special case where channels 2 to $n+1$ are identical, we have

$$\det T = T_{11} T_{22}^n \left[1 - n(T_{12} T_{21} / T_{22} T_{11}) \right] \quad (14)$$

or alternatively

$$\det T = T_{22}^{n-1} \left[T_{11} T_{22} - n T_{12} T_{21} \right] \quad (15)$$

Thus

$$Z = \frac{1}{\pi} \left[\arg T_{11} + n \arg T_{22} + \arg (1 - n T_{12} T_{21} / T_{22} T_{11}) \right] \quad (16)$$

$$\text{or} \quad Z = \frac{1}{\pi} \left[(n - 1) \arg T_{22} + \arg (T_{11} T_{22} - n T_{12} T_{21}) \right] \quad (17)$$

III. APPLICATIONS.

The relations between the matrix elements of T , defined as above (1), and the corresponding scattering potential matrix elements defined by

$$V_{ij} = \langle \varphi_i | V | \varphi_j \rangle$$

have been derived for the two channel case in {2}. If the channels are i and j

$$T_{ii} = \frac{V_{ii}(1 - V_{jj} G_j) + |V_{ij}|^2 G_j}{(1 - V_{jj} G_j)(1 - V_{ii} G_i) - |V_{ij}|^2 G_i G_j} \quad (18)$$

$$T_{ij} = \frac{V_{ij}}{(1 - V_{jj} G_j)(1 - V_{ii} G_i) - |V_{ij}|^2 G_i G_j}$$

Here, G_i, G_j are the Green's functions

$$G_j(E) = \sum_{k_j} \frac{1}{E - E_{kj} + i\delta} = F_j(E) + i \pi n_j(E)$$

where n_j is the density of states for channel j and $F_j(E)$ is its Hilbert transform.

Thus we have for the simple two channel case,

$$Z = \frac{1}{\pi} \arg \left[T_{11} T_{22} - |T_{12}|^2 \right] \quad \text{from (15) with } n = 1.$$

Substituting,

$$\begin{aligned} Z &= \frac{1}{\pi} \arg \left[\frac{[V_{11}(1-V_{22}G_2) - |V_{12}|^2G_2][V_{22}(1-V_{11}G_1) - |V_{12}|^2G_1] - |V_{12}|^2}{[(1-V_{11}G_1)(1-V_{22}G_2) - |V_{12}|^2G_1G_2]^2} \right] \\ &= \frac{1}{\pi} \arg \left[\frac{V_{11}V_{22} - |V_{12}|^2}{(1-V_{11}G_1)(1-V_{22}G_2) - |V_{12}|^2G_1G_2} \right] \\ &= \frac{-1}{\pi} \arg \left[(1 - V_{11}G_1)(1 - V_{22}G_2) - |V_{12}|^2G_1G_2 \right] \end{aligned} \quad (20)$$

We can now apply this to some physical problems.

a) Suppose the channels 1 and 2 are bands in tight binding with spin $\uparrow$ and $\downarrow$ respectively, but otherwise identical. A local scattering center is introduced, which only produces scattering processes with spin flip, i.e. $V_{\uparrow\uparrow} = V_{\downarrow\downarrow} = 0$,

Then

$$\begin{aligned} Z &= - \frac{1}{\pi} \arg \left[1 - |V_{\uparrow\downarrow}|^2 G^2 \right] \\ &= - \frac{1}{\pi} \arg \left[1 - |V_{\uparrow\downarrow}| G \right] \\ &\quad - \frac{1}{\pi} \arg \left[1 + |V_{\uparrow\downarrow}| G \right] \end{aligned} \quad (21)$$

Expressing G in terms of F and n

$$\arg (1 - |V_{\uparrow\downarrow}| G(E)) = \operatorname{arctg} \left[\frac{\pi n(E) |V_{\uparrow\downarrow}|}{1 - F(E) |V_{\uparrow\downarrow}|} \right]$$

and
$$\arg (1 + |V_{\uparrow\downarrow}| G(E)) = \operatorname{arctg} \left[\frac{-\pi n(E) |V_{\uparrow\downarrow}|}{1 + F(E) |V_{\uparrow\downarrow}|} \right]$$

So

$$\begin{aligned} Z &= -\frac{1}{\pi} \operatorname{arctg} \left[\frac{\pi |V_{\uparrow\downarrow}| n(E)}{1 - |V_{\uparrow\downarrow}| F(E)} \right] - \frac{1}{\pi} \operatorname{arctg} \left[\frac{-\pi |V_{\uparrow\downarrow}| n(E)}{1 + |V_{\uparrow\downarrow}| F(E)} \right] \\ &= -\frac{1}{\pi} \operatorname{arctg} \left[\frac{2 |V_{\uparrow\downarrow}|^2 \pi n(E) F(E)}{1 - |V_{\uparrow\downarrow}|^2 F^2(E) + \pi^2 |V_{\uparrow\downarrow}|^2 n^2(E)} \right] \end{aligned} \quad (22)$$

For a band which is degenerate n times for each direction of spin, this will be multiplied by n .

b) Returning to (20), suppose V_{11} , V_{22} and V_{12} all tend to infinity. Then

$$Z = -\frac{1}{\pi} \arg \left[1 - V_{11} G_1 - V_{22} G_2 + (V_{11} V_{22} - |V_{12}|^2) G_1 G_2 \right]$$

In the limit the last term will dominate ;

thus
$$Z = -\frac{1}{\pi} \arg \left[(V_{11} V_{22} - |V_{12}|^2) G_1 G_2 \right]$$

and as $(V_{11} V_{22} - |V_{12}|^2)$ is real,

$$\begin{aligned} Z &= -\frac{1}{\pi} \arg (G_1 G_2) = -\frac{1}{\pi} \arg G_1 - \frac{1}{\pi} \arg G_2 \\ &= -\frac{1}{\pi} \operatorname{arctg} \left[\frac{-\pi n_1(E)}{F_1(E)} \right] - \frac{1}{\pi} \operatorname{arctg} \left[\frac{-\pi n_2(E)}{F_2(E)} \right] \end{aligned} \quad (23)$$

Thus in the limit of strong potentials, the two channels are decoupled, and the charge Z is the same as in the case

$$\begin{aligned} V_{11} &\rightarrow \infty \\ V_{22} &\rightarrow \infty \\ |V_{12}|^2 &= 0 \end{aligned}$$

In appendix I, it is shown in detail that the amplitude of the tight binding wave functions at the impurity site are rigorously zero in this limit.

c) We will consider the case of a broad band overlapping a narrow band (these correspond to s and d bands respectively in transition metals) in the energy region above the top of the narrow band, but below the top of the broad band, figure 1. (Physically, this corresponds to the position of the Fermi surface in a noble metal). For convenience we will use the s, d labels for the bands.

At energy E' in figure 1, $n_d = 0$.

so $G_d(E') = F_d(E')$.

while $G_s(E') = F_s(E') - i\pi n_s(E')$.

From (20),

$$Z(E') = -\frac{1}{\pi} \operatorname{arctg} \left[\frac{\pi n_s (F_d |V_{sd}|^2 + V_{ss} (1 - V_{dd} F_d))}{(1 - V_{dd} F_d)(1 - V_{ss} F_s) - |V_{sd}|^2 F_d F_s} \right] \quad (24)$$

all parameters n, F inside the bracket being taken at E' . This is to be compared to the case of an unmixed d band ;

$$Z(E') = -\frac{1}{\pi} \arg (1 - V_{dd} G_d(E')) \quad (25)$$

As V_{dd} is increased from zero, Z stays zero until $V_{dd} F_d(E') > 1$, at which point it changes to $Z = -1$; a delta function bound d state has moved above the energy E' .

The corresponding expression when $|V_{sd}|$ is non-zero is then :

$$Z(E') = -\frac{1}{\pi} \operatorname{arctg} \left\{ \frac{\pi n_s F_d |V_{sd}|^2}{1 - (V_{dd} + |V_{sd}|^2 F_s) F_d} \right\} \quad (26)$$

the s-s scattering being neglected.

Assume that $\frac{dn_s}{dE}$ and $\frac{dF_s}{dE} \approx 0$ which seems reasonable for a broad band.

It is then possible to introduce a width $\Delta = \pi |V_{sd}|^2 n_s$ and rewrite (26) as

$$Z(E') = -\frac{1}{\pi} \arctg \left\{ \frac{\Delta}{\frac{1}{F_d(E')} - V_{eff}} \right\} \quad (27)$$

where $V_{eff} = V_{dd} + |V_{sd}|^2 F_s$ (d-d matrix element plus an energy shift due to the mixing).

From (27) it can be shown that the change in state density is :

$$\Delta n(E') = -\frac{1}{F_d^2(E')} \frac{dF_d}{dE}(E') \frac{1}{\pi} \frac{\Delta}{\left(\frac{1}{F_d(E')} - V_{eff}\right)^2 + \Delta^2} \quad (28)$$

In expression (28), $A(E') = -\frac{1}{F_d^2(E')} \frac{dF_d}{dE}(E')$ is the inverse of the amplitude at the impurity site of a d-bound state of energy E' .

Let's introduce the following functions $L(E')$ and $L_o(E')$ defined as :

$$L(E') = \frac{1}{\pi} \frac{\Delta}{\left(\frac{1}{F_d(E')} - V_{eff}\right)^2 + \Delta^2} \quad (29)$$

$$L_o(E') = \frac{1}{\pi} \frac{\Delta}{(E - E_o^d - V_{eff})^2 + \Delta^2}$$

Remark that $L_o(E')$ is a true Lorentzian centred about $E_o^d + V_{eff}$, where E_o^d is the "center of gravity" of the d-band defined by $E_o^d = \int E' n_d(E') dE'$, and $L(E')$ is some kind of "unsymmetrical" Lorentzian due to the presence of the $\frac{1}{F_d}$ term.

It is to be noted that for energies E such that $E - E_o^d \gg$ d-band width, $L(E)$ tends to the true Lorentzian since $F_d(E) \approx \frac{1}{E - E_o^d}$.

Finally, since $F_d(E')$ is a monotonically decreasing function for $E > E_{top}$, it follows from (28) that $\Delta n(E') > 0$ for energy regions such that $E > E_{top}^d$, and the conditions $\frac{dn_s}{dE} \approx 0$ $\frac{dF_s}{dE} \approx 0$ are approximately fulfilled.

The deviations from the Lorentzian shape, and the variation of $A(E)$ are connected to the details of the d-band near $E = E_{\text{top}}^d$, and need a careful analysis of the behaviour of the $F_d(E)$ function in the region $E > E_{\text{top}}^d$.

The detailed behaviour of $\Delta n(E')$ near the top of the d-band will be the subject of a next paper. Here we want simply to point out that for energies E' such that $E' - E_d^0 \gg$ d-band width, the quantity $A(E')$ tends to 1, and one finds the usual Anderson's {4} change in density of states

$$\Delta n(E') = \frac{1}{\pi} \frac{\Delta}{(E - E_c)^2 + \Delta^2}$$

where E_c is defined by $E_c = E_o^d + V_{dd} + |V_{sd}|^2 F_s$.

d) Small mixing limit.

In this calculation we neglect all powers of $|V_{sd}|$ larger or equal to 4, in order to be in the same conditions as in {2}.

We start from :

$$Z = \frac{1}{\pi} \arg \left\{ \frac{1}{1 - V_{dd}G_d - G_s G_d |V_{sd}|^2} \right\} = \frac{1}{\pi} \arg \left\{ \frac{1}{1 - V_{dd}G_d} \left[\frac{1}{1 - \frac{G_s G_d |V_{sd}|^2}{1 - V_{dd}G_d}} \right] \right\}$$

$$\approx \frac{1}{\pi} \arg \left\{ \frac{1}{1 - V_{dd}G_d} \right\} + \frac{1}{\pi} \arg \left\{ 1 + \frac{G_s G_d |V_{sd}|^2}{1 - V_{dd}G_d} \right\} \quad (31)$$

But $\frac{G_s G_d |V_{sd}|^2}{1 - V_{dd}G_d}$ is a small quantity as compared to 1 and one has :

$$\arg \left\{ 1 + \frac{G_s G_d |V_{sd}|^2}{1 - V_{dd}G_d} \right\} \approx \text{Im} \frac{G_s G_d |V_{sd}|^2}{1 - V_{dd}G_d}$$

$$\approx -\pi \frac{n_s F_d + F_s n_d - n_s V_{dd} F_d^2 - \pi^2 n_s n_d^2 V_{dd}}{|1 - V_{dd}G_d|^2} \quad (32)$$

For a broad s-band and for energies lying around the middle of it one has $n_s F_d \gg n_d F_s$.

In this situation :

$$\begin{aligned} \arg \left\{ 1 + \frac{G_s G_d |V_{sd}|^2}{1 - V_{dd} G_d} \right\} &\approx - \frac{\pi n_s}{V_{dd}} \left[F_d V_{dd} - V_{dd}^2 F_d^2 - \pi^2 n_d^2 V_{dd}^2 \right] \frac{|V_{sd}|^2}{|1 - V_{dd} G_d|^2} \\ &\approx - \frac{\pi n_s}{V_{dd}} \left[(1 - V_{dd} F_d) - |1 - V_{dd} G_d|^2 \right] \frac{|V_{sd}|^2}{|1 - V_{dd} G_d|^2} \end{aligned} \quad (33)$$

Finally, the total displaced charge in this limit reads :

$$\begin{aligned} Z = - \frac{1}{\pi} \arctg \left\{ \frac{\pi n_d V_{dd}}{1 - V_{dd} F_d} \right\} - n_s \frac{|V_{sd}|^2}{V_{dd}} \frac{1 - V_{dd} F_d}{(1 - V_{dd} F_d)^2 + (\pi V_{dd} n_d)^2} \\ + n_s \frac{|V_{sd}|^2}{V_{dd}} \end{aligned} \quad (34)$$

which is exactly the formula derived in {2} by another method.

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REFERENCES

- 1) Blandin A., Thesis Paris (1961)
- 2) Gomes A.A., J . Phys. Chem. Sol. 27, 451, (1966)
- 3) Toulouse G., Sol. Stat. Comm., 4, 593, (1966)
- 4) Anderson P.W., Phys. Rev., 124, 41, (1961)

Appendix I

The scattered wave function in the two channel case is given by {2}

$$\begin{aligned} \psi_i^+ = \phi_i + \frac{V_{ii}(i-V_{jj}G_j) + |V_{ij}|^2 G_j}{(1-V_{ii}G_i)(1-V_{jj}G_j) - |V_{ij}|^2 G_i G_j} \sum_{k_i'} \frac{\phi_i(k_i')}{\epsilon - \epsilon_{k_i'} + i\delta} \\ + \frac{V_{ji}}{(1-V_{ii}G_i)(1-V_{jj}G_j) - |V_{ij}|^2 G_i G_j} \sum_{k_j'} \frac{\phi_j(k_j')}{\epsilon - \epsilon_{k_j'} + i\delta} \end{aligned} \quad (A 1)$$

In the limit of an infinite potential one gets :

$$\psi_i^+(\infty) = \phi_i - \frac{1}{G_i} \sum_{k_i'} \frac{\phi_i(k_i')}{\epsilon - \epsilon_{k_i'} + i\delta} \quad (A 2)$$

Expression (A 2) shows that in this limit the wave functions belonging to channel j are not mixed to those of channel i, thus showing explicitly that an infinite potential decouples channels i and j. If ϕ_i may be described by a tight binding approximation, the amplitude of the scattered wave at the central site is given by

$$\langle 0 | \psi_i^+(\infty) \rangle = 1 - \frac{1}{G_i} \sum_{k_i'} \frac{1}{\epsilon - \epsilon_{k_i'} + i\delta} = 1 - \frac{1}{G_i} G_i = 0 \quad (A 3)$$

thus showing that the amplitude is rigorously zero.

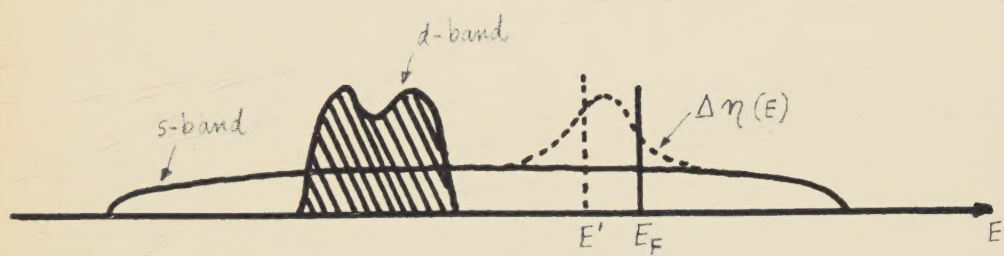


fig 1

